

IONIC EQUILIBRIUM

4.0 INTRODUCTION

Formulae :

$$(i) \quad \ln x = \log_e x = 2.303 \log_{10} x = 2.303 \log x$$

$$(ii) \quad \log (x \times y) = \log x + \log y$$

$$(iii) \quad \log \left(\frac{x}{y} \right) = \log x - \log y$$

$$(iv) \quad \log x^y = y \log x$$

$$\begin{aligned} \text{Ex. (i)} \quad \log 6 &= \log (2 \times 3) \\ &= \log 2 + \log 3 \\ &= 0.3010 + 0.4771 = 0.7781 \end{aligned}$$

$$\begin{aligned} (ii) \quad \log 30 &= \log (3 \times 10) \\ &= \log 3 + \log 10 \\ &= \log 0.4771 + 1 = 1.4771 \end{aligned}$$

$$\begin{aligned} (iii) \quad \log 1000 &= \log 10^3 \\ &= 3 \log 10 = 3 \times 1 = 3 \end{aligned}$$

A. Some values of Log :

$$\log 1 = 0$$

$$\log 2 = 0.3010$$

$$\log 3 = 0.4771$$

$$\log 4 = 0.6020$$

$$\log 5 = 0.699$$

$$\log 6 = 0.7781$$

$$\log 7 = 0.8451$$

$$\log 8 = 0.9030$$

$$\log 9 = 0.9542$$

$$\log 10 = 1$$

$$\log 11 = 1.04$$

$$\log 100 = 2$$

$$\log 1000 = 3$$

Some terms which are used in ionic equilibrium : **Antilog :** $\text{Antilog}(x) = 10^x$

$$\text{Ex. Antilog}(2) = 10^2 = 100$$

$$\text{Antilog}(0.3010) = 10^{0.3010} = 2$$

$$\text{Antilog}[\log(2)] = \text{Antilog}(0.3010) = 2$$

pH - Scale : Given by – **Sorenson**

pH Scale is called Sorenson scale.

pH scale is a measuring scale used to measure strength of acid and base and its value is equal to $-\log[H^+]$

$$\text{i.e.} \quad \text{pH} = -\log[H^+] = \log \frac{1}{[H^+]}$$

$$\begin{aligned} \text{Ex.} \quad [H^+] &= 10^{-3} \\ \text{pH} &= -\log 10^{-3} = +3 \log 10 = 3 \end{aligned}$$

Conclusion :

If $\text{pH} = x$ then $[H^+] = 10^{-x}$ or Vice versa

i.e. If $[H^+] = 10^{-x}$ then $\text{pH} = x$

$$\text{pOH} \rightarrow \text{It is equal to } -\log [OH^-] \text{ i.e. } \text{pOH} = -\log [OH^-] = \log \frac{1}{[OH^-]}$$

$$\text{Ex. If } X = \frac{a}{b} \times 10^{-c}, \text{ then find pX ?}$$

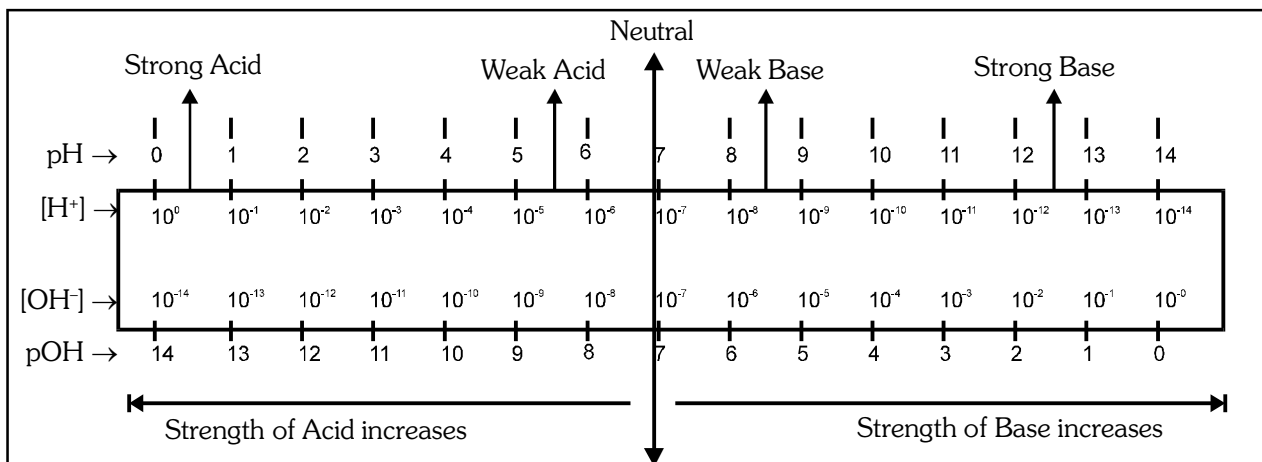
$$\text{Sol. } \text{pX} = -\log X = -\log \left(\frac{a}{b} \times 10^{-c} \right)$$

$$\text{pX} = - \left[\log \frac{a}{b} + \log 10^{-c} \right] = -[\log a - \log b - c]$$

$$\boxed{\text{pX} = c + \log b - \log a}$$



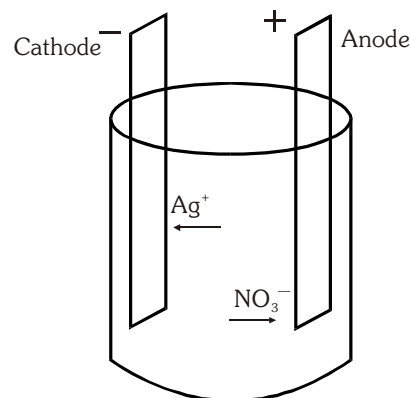
pH scale at 25°C



According to conductivity substances are of two types:

- (1) **Non-Conductor** - Those substances which do not show the flow of current or electricity.
Ex. Non - metals, plastic, rubber, wood etc.
Exception - Graphite is a non-metal but show conductivity due to motion of free electrons.
- (2) **Conductors** - Those substances which show conductivity or flow of current are called conductors and these are of two types :
 - (a) **Metallic conductor** - Those conductor which show conductivity due to motion of free electrons.
Ex. All metals, Graphite
 - (b) **Ionic conductors** -

Those conductor which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode). Due to this reason, they are called cations and anions respectively. The current flows through the solution due to the movement of the ion. Movement of ions through the solution of electrolyte ($AgNO_3$) towards oppositely charged electrodes.



According to strength, ionic conductors are of two types -

- (1) **Strong electrolytes** - Those ionic conductors which are **completely ionized in aqueous solution** are called as strong electrolytes.
 For strong electrolyte the value of degree of ionisation is 100% i.e. $\alpha = 1$
Ex. (a) Strong acid $\rightarrow H_2SO_4, HCl, HNO_3, HClO_4, HBr, HI$
 (b) Strong base $\rightarrow KOH, NaOH, Ba(OH)_2, CsOH, RbOH$
 (c) All Salts $\rightarrow NaCl, KCl, CuSO_4, \dots$
- (2) **Weak electrolytes** - Those electrolytes which are **partially ionized in aqueous solution** are called as weak electrolytes. For weak electrolytes the value of α is less than one.
Ex. (a) Weak acids $\rightarrow HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, B(OH)_3$, etc.

\downarrow
 H_3BO_3
 (Boric acid)

 (b) Weak bases $\rightarrow NH_4OH, Cu(OH)_2, Zn(OH)_2, Fe(OH)_3, Al(OH)_3$ etc.



4.1 ARRHENIUS CONCEPT :

- (a) According to Arrhenius when an electrolyte dissolves in water it splits up into two oppositely charged particles i.e. cation and anion.
- (b) In an electrolytic solution (Aqueous solution of electrolyte), total +ve charge is equal to total -ve charge i.e. solution is electrically neutral.
 \Rightarrow In an electrolytic solution number of +ve ions may or may not be equal to the number of negative ions.
- (c) Properties of an electrolytic solution are defined by its ions.
- Ex.** Blue colour of CuSO_4 aqueous solution is due to Cu^{+2} ion (dark blue colour)
- (d) When electric current is pass in aqueous solution of electrolyte then cation shows migration towards cathode where as anion shows migration towards anode.
- (e) When a weak electrolyte is dissolved in water an equilibrium is set up between unionized moles and ionized moles.

This condition of the reversible ionic reaction is known as ionic equilibrium. $\text{AB (Aq.)} \rightleftharpoons \text{A}^+(\text{Aq.}) + \text{B}^-(\text{Aq.})$

According to L.M.A.

$$\text{Ionisation constant } K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

Illustrations

Illustration 1 If $[\text{H}^+] = \frac{5}{3} \times 10^{-4}$ then find pH ?

Solution $\text{pH} = -\log [\text{H}^+] = -\log \left(\frac{5}{3} \times 10^{-4} \right)$

$$= - \left[\log \frac{5}{3} + \log 10^{-4} \right] = - [\log 5 - \log 3 - 4]$$

$$= - [0.699 - 0.4771 - 4] = - [-3.778] = 3.778$$

Illustration 2 **Assertion :** H_2SO_4 is a strong acid.

Reason : H_2SO_4 undergoes almost completely ionised in aqueous solution.

(1) A

(2) B

(3) C

(4) D

Solution **Ans. (1)**

4.2 OSTWALD'S DILUTION LAW

\Rightarrow Ostwald dilution law is applicable only for weak electrolytes.

Statement : According to Ostwald when solution of weak electrolyte is diluted then degree of ionisation of solution is increased, is called dilution law.

Let $\text{AB (Aq.)} \rightleftharpoons \text{A}^+(\text{Aq.}) + \text{B}^-(\text{Aq.})$

Initial concentration $\frac{C}{C} \quad 0 \quad 0$

Degree of ionisation (α) $(C - C\alpha) \quad (C\alpha) \quad (C\alpha)$

According to L.M.A.

Ionisation constant $K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}; K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

If $\alpha \ll 1$ then $1 - \alpha \simeq 1$

$$K = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad (K = \text{constant, At constant temperature})$$

$$\alpha \propto \frac{1}{\sqrt{C}} \quad (C \propto \frac{1}{V}) \quad \alpha \propto \sqrt{V}$$



volume \equiv dilution $\alpha \propto \sqrt{\text{dilution}}$ by dilution law
 dilution \uparrow $\alpha \uparrow$
 At infinite dilution, $\alpha = 100\%$

Thus for weak electrolytes the degree of ionisation is directly proportional to square root of dilution or inversely proportional to square root of concentration. This law is known as Ostwald Dilution Law.

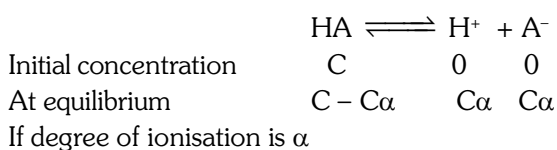
GOLDEN KEY POINTS

- At infinite dilution the value of α becomes equal to one.
- The value of concentration should be in terms of normality for calculation of pH.

Application of Ostwald's Dilution Law : $K = C\alpha^2$

(a) For mono basic weak acid (HA)

(i). Ionisation constant (K_a)



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

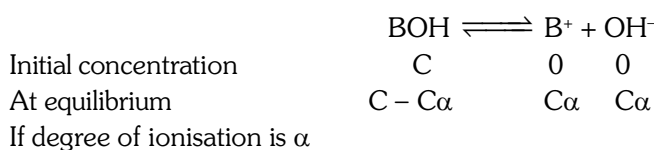
$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha \ll \ll \ll 1 \quad \therefore (1-\alpha) \approx 1$$

$$\therefore K_a = C\alpha^2$$

(b) For mono acidic weak base (BOH)

Ionisation constant (K_b)



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

$$K_b = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\because \alpha \ll \ll \ll 1 \quad \therefore (1-\alpha) \approx 1$$

$$\therefore K_b = C\alpha^2$$

Where

$K_a \rightarrow$ Ionisation constant of weak acid
 $K_b \rightarrow$ Ionisation constant of weak base } Both K_a and K_b depends only on temperature

(ii). $[\text{H}^+]$ (Concentration of H^+)

$$[\text{H}^+] = C\alpha \quad \dots\dots(1)$$

$$K_a = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} \quad \dots\dots(2)$$

$$\text{from Eq. (1) and (2) } [\text{H}^+] = C \times \frac{\sqrt{K_a}}{\sqrt{C}}$$

$$[\text{H}^+] = \sqrt{K_a \times C}$$

(iii). $\text{pH} = -\log [\text{H}^+]$

put the value of $[\text{H}^+]$

$$\text{pH} = -\log(\sqrt{K_a \times C}) = -\log(K_a \times C)^{1/2}$$

$$\text{pH} = -\frac{1}{2}[\log K_a + \log C]$$

$$\text{pH} = -\frac{1}{2}\log K_a - \frac{1}{2}\log C$$

$$\text{pH} = \frac{1}{2}\text{p}K_a - \frac{1}{2}\log C$$

$[\text{OH}^-]$ (Concentration of OH^-)

$$[\text{OH}^-] = C\alpha \quad \dots\dots(1)$$

$$K_b = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_b}{C}} \quad \dots\dots(2)$$

$$\text{from Eq. (1) and (2) } [\text{OH}^-] = C \times \frac{\sqrt{K_b}}{\sqrt{C}}$$

$$[\text{OH}^-] = \sqrt{K_b \times C}$$

$\text{pOH} = -\log [\text{OH}^-]$

put the value of $[\text{OH}^-]$

$$\text{pOH} = -\log(\sqrt{K_b \times C}) = -\log(K_b \times C)^{1/2}$$

$$\text{pOH} = -\frac{1}{2}[\log K_b + \log C]$$

$$\text{pOH} = -\frac{1}{2}\log K_b - \frac{1}{2}\log C$$

$$\text{pOH} = \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$



In summary :

1. $K_a = C\alpha^2$

2. $[H^+] = C\alpha = \sqrt{K_a \times C}$

3. $pH = -\log [H^+]$

or $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$

1. $K_b = C\alpha^2$

2. $[OH^-] = C\alpha = \sqrt{K_b \times C}$

3. $pOH = -\log [OH^-]$

or $pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C$

Limitation of Ostwald Dilution Law :

It is not applicable for strong electrolytes.

Factors affecting the Value of Degree of ionisation :

(1) Temperature \rightarrow On increasing temperature, ionization increases so α increases because dissociation is endothermic process.

(2) Dilution $\rightarrow \alpha \propto \sqrt{V}$ so on dilution, α increases.

(3) Nature of electrolytes

(i) Strong electrolytes

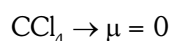
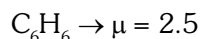
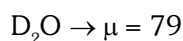
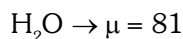
$$\alpha = 100\%$$

(ii) Weak electrolytes

$$\alpha < 100\%$$

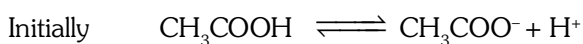
(4) Nature of solvent

If Dielectric constant μ of solvent increases then the value of α increases.

**Mixing of ions :**

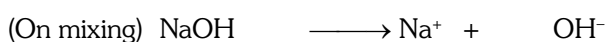
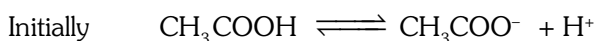
(a) Common ion effect	(b) Odd ion effect
When a strong electrolyte having a common ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is decreased. This effect is called common ion effect.	When a strong electrolyte having a odd ion, is mixed with weak electrolyte then the degree of ionisation (α) of weak electrolyte is increased. This effect is called odd ion effect.

Common ion : On mixing CH_3COONa with CH_3COOH solution



(On mixing) $CH_3COONa \longrightarrow CH_3COO^- + Na^+$; $[CH_3COO^-]$ increases so $[H^+]$ decreases respectively.

Odd ion : On mixing, $NaOH$ with CH_3COOH solution



Due to odd ion effect $H^+ + OH^- \rightarrow \text{Water}$



Illustrations

Illustration 3 For which, dilution law is applicable :

- | | |
|---------------------------------------|--------------|
| (1) NaCl (SASB salt) | (2) HCl (SA) |
| (3) CH ₃ COONa (WASB salt) | (4) None |

Solution **Ans. (4)**

Illustration 4 Find out the value of α of 10^{-2} M HCN solution if $[H^+] = 10^{-3}$.

Solution $[H^+] = C\alpha$

$$10^{-3} = 10^{-2}\alpha \text{ or } \alpha = \frac{10^{-3}}{10^{-2}} = 10^{-1} \text{ or } \alpha = 0.1$$

$$\alpha = 10\%$$

Illustration 5 For 10 M CH₃COOH solution if $K_a = 10^{-5}$ then find out :

- (i) α (ii) $[H^+]$ (iii) pH

Solution (i) α

(Degree of ionisation) $\therefore K_a = C\alpha^2$

$$10^{-5} = 10\alpha^2 \text{ or } \alpha^2 = \frac{10^{-5}}{10} = 10^{-6} \text{ or } \alpha = 10^{-3}$$

(ii) $[H^+] = C\alpha = 10 \times 10^{-3} = 10^{-2}$

(iii) $pH = -\log [H^+] = -\log 10^{-2} = 2$

Illustration 6 For 10^{-3} M H₂CO₃ if $\alpha = 10\%$ then find out the value of pH ?

Solution Normality = M \times V.F. = $10^{-3} \times 2 = 2 \times 10^{-3}$

$$[H^+] = C\alpha = 2 \times 10^{-3} \times 0.1 = 2 \times 10^{-4}$$

$$pH = -\log [H^+] = -\log (2 \times 10^{-4}) = -\log 2 - \log 10^{-4} = -0.3010 + 4 = 3.7$$

Illustration 7 **Assertion :** NaCl + HCl does not experience common ion effect.

Reason : Both NaCl and HCl are strong electrolytes.

- (1) A (2) B (3) C (4) D

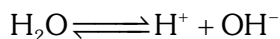
Solution **Ans. (1)**

4.3 EXPLANATION OF WATER

- a. Nature of water is neutral. $[H^+] = [OH^-] [=10^{-7}\text{M (at } 25^\circ\text{C)}]$
i.e. at 25°C $pH = 7$ and $pOH = 7$
 $\therefore pH = pOH$
- b. No. of H₂O moles in 1 litre water = $\frac{1000}{18} = 55.5$ moles
- c. Molar concentration of H₂O = 55.5 mol L^{-1}
- d. Number of H₂O molecules in 1 litre water = $55.5 N_A$ (N_A = AVOGADRO'S NUMBER)
- e. Concentration of H⁺ and OH⁻ ions in 1 litre water
 $[H^+] = 10^{-7} \text{ mol L}^{-1}$ and $[OH^-] = 10^{-7} \text{ mol L}^{-1}$
- f. No. of H⁺ and OH⁻ ions in 1 litre water
No. of H⁺ ions = $10^{-7}N_A$ and No. of OH⁻ ions = $10^{-7}N_A$
- g. In water (Number of H₂O molecules : Number of H⁺ ions)
 $= 55.5 N_A : 10^{-7}N_A$
 $= 55.5 \times 10^7 : 1$
i.e. one H⁺ ion is obtained from $55.5 \times 10^7 \text{ H}_2\text{O}$ molecules



h. Degree of ionisation of water (α) :



According to Ostwald's dilution law

$$[\text{H}^+] = c \alpha$$

$$\alpha = \frac{10^{-7}}{55.5} = 1.8 \times 10^{-9}$$

$$\boxed{\alpha = 1.8 \times 10^{-7}\%}$$

Hence, water is a very weak electrolyte.

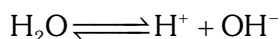
i. K (Ionisation constant of water) :



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K = \frac{10^{-7} \times 10^{-7}}{55.5} \quad \text{or} \quad \boxed{K = 1.8 \times 10^{-16}}$$

j. Ionic product of water K_w :



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Since, dissociation takes place to a very small extent, $[\text{H}_2\text{O}]$ may be regarded as constant.

Thus, the product $K \cdot [\text{H}_2\text{O}]$ gives another constant which designated as K_w . So,

$$\boxed{K_w = [\text{H}^+][\text{OH}^-]}$$

$$\text{At } 25^\circ\text{C} - K_w = 10^{-7} \times 10^{-7} = 10^{-14}$$

$$K [\text{H}_2\text{O}] = K_w \Rightarrow \boxed{K_w > K} \quad (\text{always})$$

Various forms of K_w

(a) $K_w = [\text{H}^+][\text{OH}^-]$ for water $[\text{H}^+] = [\text{OH}^-]$

(b) $K_w = [\text{H}^+]^2$

(c) $K_w = [\text{OH}^-]^2$

(d) $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

(e) $K_w = [\text{H}_3\text{O}^+]^2 \quad \{[\text{H}_3\text{O}^+] = [\text{H}^+]\}$
Hydronium ion Proton

• Relation in between pH and pOH :

$$K_w = [\text{H}^+][\text{OH}^-]$$

taking $-\log$ on both sides

$$-\log K_w = -\log [\text{H}^+] - \log [\text{OH}^-]$$

$$\boxed{\text{p}K_w = \text{pH} + \text{pOH}}$$



- Nature of water is neutral so,
[pH = pOH]

$$pK_w = pH + pOH$$

$$2pH = pK_w$$

$$pH = \frac{pK_w}{2}$$

$$pH = pOH = \frac{pK_w}{2}$$

$$pK_w = pOH + pOH$$

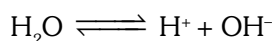
$$2 pOH = pK_w$$

$$pOH = \frac{pK_w}{2}$$

At 25°C, $K_w = 10^{-14}$ or $pK_w = 14$

$\therefore pH + pOH = 14$ or $pH = pOH = 7$

k. Effect of temperature :-



Ionization of water is endothermic process so, on increasing temperature α increases or $[H^+]$ and $[OH^-]$ increases or $[H^+][OH^-]$ increases i.e. K_w increases means pH decreases or pOH decreases.

$$T \uparrow = \alpha \uparrow = [H^+] [OH^-] \uparrow = K_w \uparrow \Rightarrow pK_w \downarrow$$

At 25°C, $K_w = 10^{-14}$

At 90°C, $K_w = 10^{-12}$

Parameters	At 25°C	At 90°C
K_w	10^{-14}	10^{-12}
pK_w	14	12
$pH = \frac{pK_w}{2} = pOH$	7	6
$[H^+] = [OH^-] = \sqrt{K_w}$	10^{-7}	10^{-6}
$pH + pOH = pK_w$	14	12

GOLDEN KEY POINTS

- On increasing temperature, both $[H^+]$ and $[OH^-]$ increases equally so water remains neutral but neutral pH changes from 7 to 6 at 90°C.

Illustrations

Illustration 8 Dissociation constant of water at 25°C is

(1) $10^{-14} \times (55.5)^{-1}$

(2) $10^{-7} \times (18)^{-1}$

(3) $10^{-14} \times (18)^{-1}$

(4) $10^{-7} \times (55.4)^{-1}$

Solution **Ans. (1)**

Illustration 9 What should be the number of H^+ ions in 1 mL of distilled water, if the number of H^+ ions in 1 L is 6.023×10^{16} ?

Solution Number of H^+ ions in 1 mL distilled water = $\frac{6.023 \times 10^{16}}{1000} = 6.023 \times 10^{13}$

BEGINNER'S BOX-1

- The pH of a 0.005 M H_2SO_4 solution is—
(1) 3.3 (2) 5.0 (3) 2.0 (4) 4.0
- If pure water has $pK_w = 13.36$ at 50°C, the pH of pure water will be—
(1) 6.68 (2) 7.0 (3) 7.13 (4) 6.0

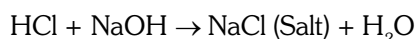
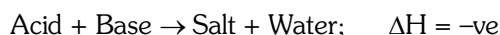


3. How many H^+ ions are present in 1 ml of a solution whose pH is 13 ?
 (1) 10^{-16} (2) 6.022×10^{13} (3) 6.022×10^7 (4) 6.022×10^{23}
4. The pH of solutions A, B, C and D are 9.5, 2.5, 3.5 and 5.5 respectively. The most acidic solution is—
 (1) D (2) C (3) A (4) B
5. Calculate the concentration of the formate ion present in 0.100 M formic acid ($HCOOH$) solution at equilibrium ($K_a = 1.7 \times 10^{-4}$).
 (1) 4.1×10^{-3} M (2) 3.1×10^{-3} M (3) 2.1×10^{-3} M (4) 5.1×10^{-3} M
6. Which of the following is the weakest acid ?
 (1) Phenol ($K_a = 1.3 \times 10^{-10}$) (2) Hydrocyanic acid ($K_a = 4.9 \times 10^{-10}$)
 (3) Acetic acid ($K_a = 1.8 \times 10^{-5}$) (4) Benzoic acid ($K_a = 6.5 \times 10^{-5}$)
7. The pH of 0.1 M monobasic acid is 4.50. The acidity constant (K_a) of the monobasic acid is—
 (1) 1.0×10^{-7} (2) 1.0×10^{-5} (3) 1.0×10^{-4} (4) 1.0×10^{-8}
8. Which of the following is the strongest base ?
 (1) $C_6H_5NH_2$ ($pK_b = 9.42$) (2) $C_6H_5NHCH_3$ ($pK_b = 9.15$)
 (3) $C_6H_5N(CH_3)_2$ ($pK_b = 8.94$) (4) $C_6H_5NHC_2H_5$ ($pK_b = 8.89$)
9. Value of dissociation constant of acetic acid is 10^{-6} , where as dissociation constant of formic acid is 10^{-5} . Which of the following will be the value of pK_a (acetic acid) - pK_a (formic acid)
 (1) 10 (2) +1 (3) 10^{-1} (4) -1
10. A solution has pOH equal to 13 at 298 K. The solution will be
 (1) highly acidic (2) highly basic (3) moderately basic (4) unpredictable
11. What would be $[H^+]$ of 0.006 M benzoic acid ($K = 6 \times 10^{-5}$)
 (1) 0.6×10^{-4} (2) 6×10^{-4} (3) 6×10^{-3} (4) 3.6×10^{-4}

4.4 SALTS, TYPES OF SALT AND CONJUGATE THEORY

(A) **SALT** : Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds.

i.e. A compound formed by the combination of acid and base is known as salt.



(B) TYPES OF SALT

(a) **Normal/general salts** :- The salts formed by the loss of all possible protons. (replaceable hydrogen ions as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen ion or a hydroxyl (OH^-) group.

Ex.: $NaCl$, $NaNO_3$, K_2SO_4 , $Ca_3(PO_4)_2$, Na_2HPO_3 , NaH_2PO_2 etc.

(b) **Acid salts** :- Salts formed by incomplete neutralisation of poly basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen ions (H^+).

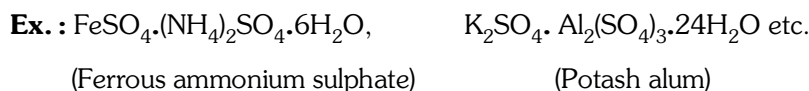
Ex.: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4 , Na_2HPO_4 etc.

(c) **Basic salts** :- Salts are formed by incomplete neutralisation of poly acidic base are called basic salts. Such salts still contain one or more hydroxyl ion group.

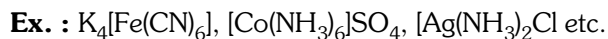
Ex.: $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.



- (d) **Double salts :-** The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only i.e. when dissolved in water they break into simple ions.

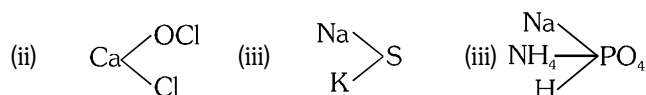
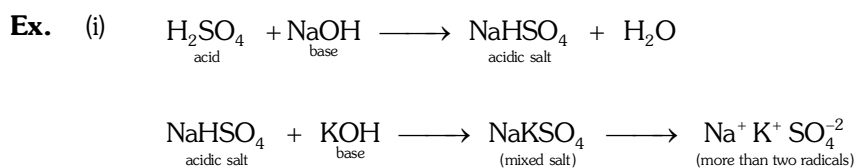


- (e) **Complex salts :-** These salts when dissolved in water give complex ions. Complex ions are stable in solid state as well as in solutions.



- (f) **Mixed salts :-** The salts which furnishes more than one type of cations or more than one type of anions when dissolved in water are called mixed salts.

These are formed by the neutralisation of more than one acids and bases.

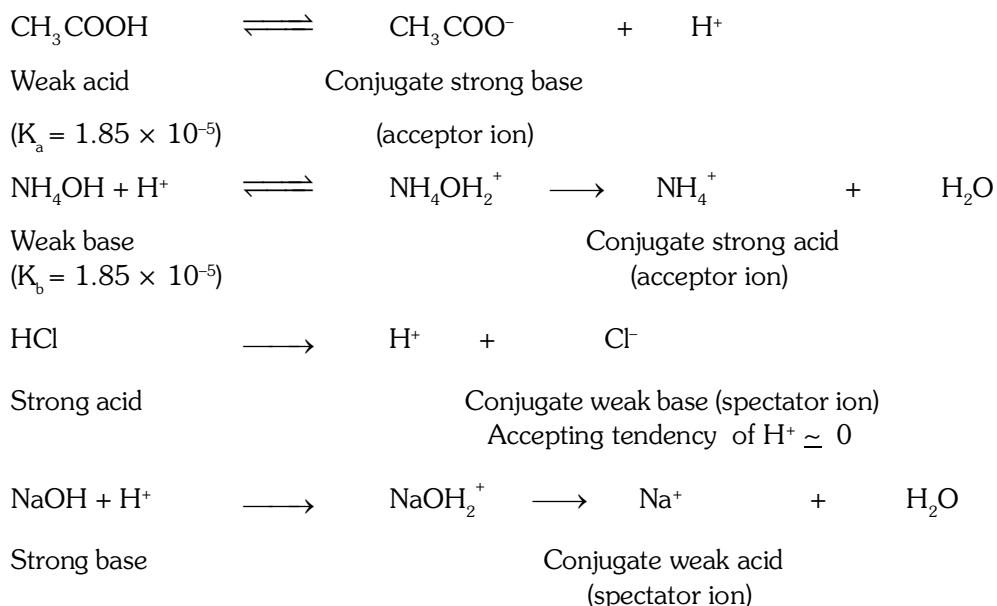


(a) Types of general salts :

- (i) SASB (ii) SAWB (iii) WASB (iv) WAWB

(C) Conjugate acid-base pair :

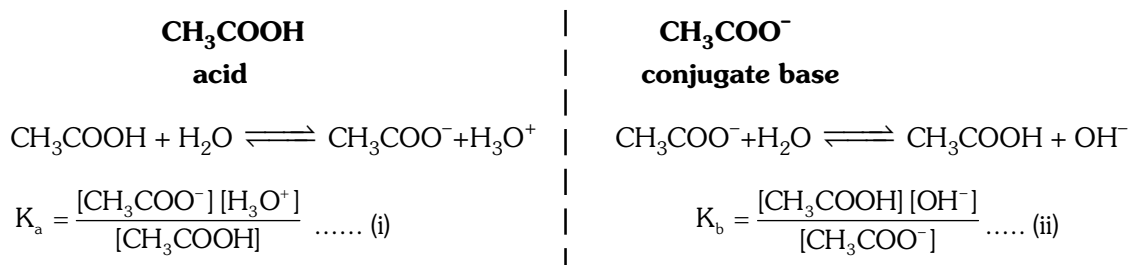
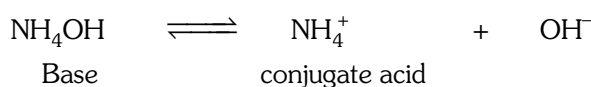
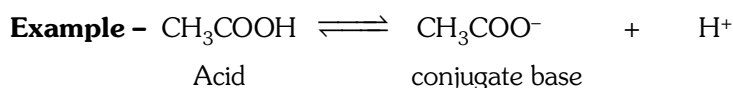
- (i) Conjugate acid-base pairs means difference between two species of only one H^+ ion.
(ii) When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore it behaves as a base.



Note : Strong acids have weak conjugate bases while weak acids have strong conjugate bases. Similarly, strong bases have weak conjugate acids while weak bases have strong conjugate acids.



(D) Relation between conjugate acid-base pair :-



In both the reactions H_2O in excess quantity so active mass of H_2O is one.

Now multiply the equation (i) and (ii)

$$K_a \times K_b = [\text{H}^+][\text{OH}^-]$$

we know $[\text{H}^+] \times [\text{OH}^-] = K_w$ (Ionic product of water)

$K_a \times K_b = K_w$

Taking $-\log$ on both sides

$\text{p}K_a + \text{p}K_b = \text{p}K_w$

we know that for water at 25°C ,

$$K_w = 10^{-14} \text{ or } \text{p}K_w = 14$$

So

$K_a \times K_b = 10^{-14}$

 or

$\text{p}K_a + \text{p}K_b = 14$

Above relation is applicable only for conjugate acid-base pairs.

Illustrations

Illustration 10 Which salt is not an example of acidic salt :-

(1) HCOONa

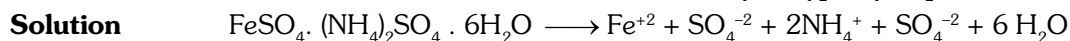
(2) NaH_2PO_2

(3) NaHS

(4) (1) and (2) both

Solution **Ans. (4)**

Illustration 11 Calculate the no. of ions in Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ or Ferrous Ammonium Sulphate



Total number of ions = 5

4.5. HYDROLYSIS OF SALTS

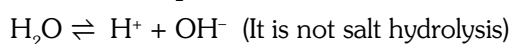
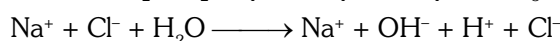
Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.



(A) Hydrolysis of strong acid and strong base [SA - SB] types of salt -

Ex. NaCl , BaCl_2 , Na_2SO_4 , KClO_4 , BaSO_4 , NaNO_3 , KBr , KCl etc.

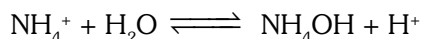
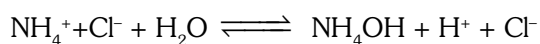
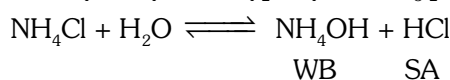


- (i) Hydrolysis of salt of [SA - SB] is not possible as both cation and anion are not reactive.
- (ii) Aqueous solution of these type of salt is neutral in nature. ($\text{pH} = \text{pOH} = 7$)
- (iii) pH of the solution is 7.
- (iv) No effect on litmus paper.



(B) Hydrolysis of strong acid and weak base [SA - WB] types of salt -

Ex. $\text{CaSO}_4, \text{NH}_4\text{Cl}, (\text{NH}_4)_2\text{SO}_4, \text{Ca}(\text{NO}_3)_2, \text{ZnCl}_2, \text{CuCl}_2, \text{CaCl}_2, \text{AgCl}, \text{AgI}, \text{AgNO}_3$ etc



- (i) In this type of salt hydrolysis, cation reacts with H_2O therefore called as cationic hydrolysis. The cation of the salt which has come from weak base is reactive.
- (ii) Solution is acidic in nature as $[\text{H}^+]$ is increased.
- (iii) pH of the solution is less than 7.
- (iv) Solution turns blue litmus paper red.

K_h = Hydrolysis constant

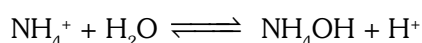
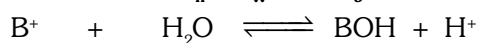
K_w = Ionic product of water

K_a = Ionisation constant of acid

K_b = Ionisation constant of base

h = Degree of hydrolysis

C = Concentration of salt (concentration of ions)

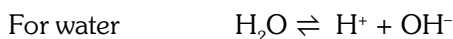
(a) Relation between K_h , K_w and K_b 

Hydrolysis constant $[K_h]$

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \dots\dots(1)$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots\dots(2)$$



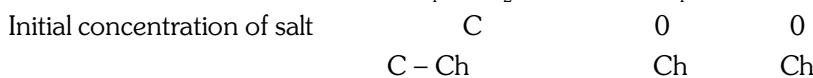
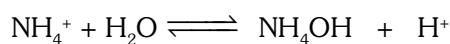
$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots\dots(3)$$

Now multiplying Eq. (1) and (2) = Eq. (3)

$$\frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = [\text{H}^+][\text{OH}^-]$$

i.e. $K_h \times K_b = K_w$

$$\boxed{K_h = \frac{K_w}{K_b}} \quad \dots\dots(4)$$

(b) Degree of hydrolysis - Represented by h 

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2 h^2}{C(1 - h)} = \frac{Ch^2}{(1 - h)}$$

Since $h \ll 1$ then $(1 - h) \approx 1$



$$\therefore \boxed{K_h = Ch^2} \quad \dots\dots(5)$$

$$h^2 = \frac{K_h}{C} \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}} \quad \dots\dots(6)$$

$$\therefore K_h = \frac{K_w}{K_b} \quad \Rightarrow \quad h = \sqrt{\frac{K_w}{K_b C}}$$

$$h = \sqrt{\frac{K_w}{K_b \times C}} \quad \dots\dots(7)$$

(c) pH of the solution : $\text{pH} = -\log [\text{H}^+]$

$$[\text{H}^+] = Ch = C \sqrt{\frac{K_w}{K_b \times C}} \quad \Rightarrow \quad [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}} \quad \dots\dots(8)$$

taking - log on both sides

$$-\log [\text{H}^+] = -\log \sqrt{\frac{K_w \times C}{K_b}} \quad \Rightarrow \quad \text{pH} = -\log \left(\frac{K_w \times C}{K_b} \right)^{1/2}$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log C - \log K_b]$$

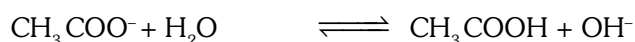
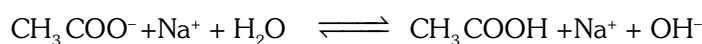
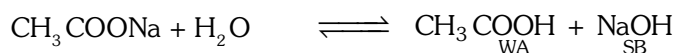
$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log C - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C} \quad \dots\dots(9)$$

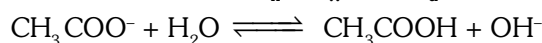
(C) Hydrolysis of weak acid and strong base [WA – SB] types of salt –

Ex. CH_3COONa , HCOONa , KCN , NaCN , K_2CO_3 , BaCO_3 , K_3PO_4 etc.



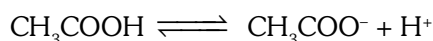
- (i) In this type of salt hydrolysis, anion reacts with water therefore called as anionic hydrolysis. The anion of the salt which has come from weak acid is reactive.
- (ii) Solution is basic in nature as $[\text{OH}^-]$ increases.
- (iii) pH of the solution is greater than 7.
- (iv) Solution turns red litmus paper blue.

(a) Relation between K_h , K_w and K_a



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots\dots(1)$$

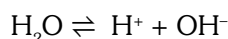
For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \dots\dots(2)$$



For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \dots\dots\dots(3)$$

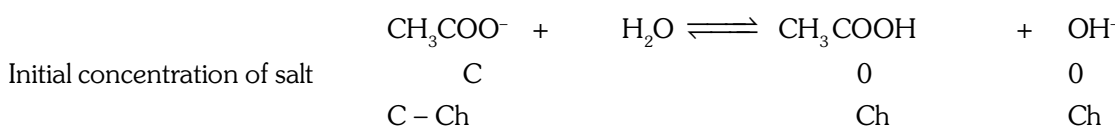
Now multiply eq. (1) \times eq. (2) = eq. (3)

$$\frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_a = K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}} \quad \dots\dots\dots(4)$$

(b) Degree of hydrolysis (h) :



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2 h^2}{C(1 - h)}$$

$$K_h = \frac{Ch^2}{(1 - h)}$$

Since $h \ll 1$ then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = Ch^2} \quad \dots\dots\dots(5)$$

$$h^2 = \frac{K_h}{C} \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}} \quad \dots\dots\dots(6)$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}} \quad \dots\dots\dots(7)$$

(c) pH of the solution

$$[\text{OH}^-] = Ch$$

$$[\text{OH}^-] = C \times \sqrt{\frac{K_w}{K_a \times C}} \quad \text{or} \quad [\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}} \quad \dots\dots\dots(8)$$

taking - log on both sides

$$-\log [\text{OH}^-] = -\log \left(\frac{K_w \cdot C}{K_a} \right)^{1/2}$$

$$\text{pOH} = -\frac{1}{2} [\log K_w + \log C - \log K_a]$$

$$\text{pOH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C \quad \text{or} \quad \text{pOH} = 7 - \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$$

$$\therefore \text{pH} + \text{pOH} = 14$$

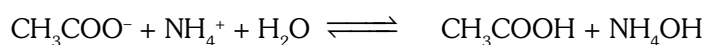
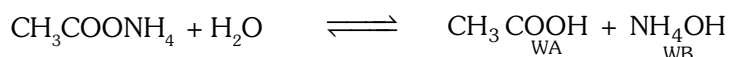
$$\text{pH} = 14 - \text{pOH}$$

$$\therefore \text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C \quad \dots\dots\dots(9)$$



(D) Hydrolysis of weak acid and weak base (WA - WB) type of salt :

Ex. $\text{CH}_3\text{COONH}_4$, AgCN , NH_4CN , CaCO_3 , $[\text{NH}_4]_2\text{CO}_3$, ZnHPO_3 etc.

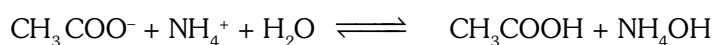


- (i) Maximum hydrolysis occurs of the salt of (WA – WB) as both the cation and anion are reactive.
- (ii) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid base
- (iii) pH of the solution is near to 7.

For WA - WB types of salt :

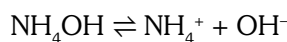
Terms	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	$\text{pH} < 7$	$\text{pH} > 7$	$\text{pH} = 7$

(a) Relation between K_h , K_w , K_a and K_b



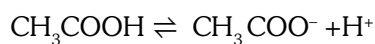
$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \quad \text{.....(1)}$$

For weak base



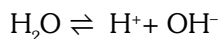
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{.....(2)}$$

For weak acid



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \quad \text{.....(3)}$$

For water



$$K_w = [\text{H}^+][\text{OH}^-] \quad \text{.....(4)}$$

Multiply Eq. (1) \times Eq. (2) \times Eq. (3) = Eq. (4)

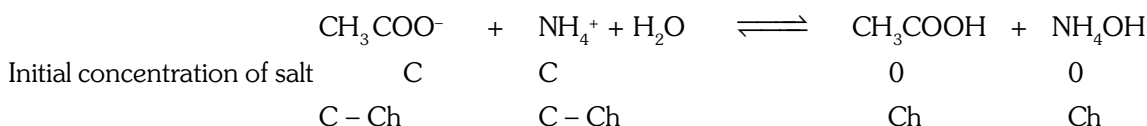
$$\frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b} \quad \text{.....(5)}$$



(b) Degree of hydrolysis (h) –



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} = \frac{\text{Ch} \times \text{Ch}}{(C - \text{Ch})(C - \text{Ch})} = \frac{C^2 h^2}{C(1-h) \times C(1-h)}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$$\therefore \boxed{K_h = h^2} \quad \text{.....(6)}$$

$$\text{or } h^2 = \frac{K_w}{K_a \times K_b} \quad \text{or } \boxed{h = \sqrt{\frac{K_w}{K_a \times K_b}}} \quad \text{.....(7)}$$

(c) pH of the solution

from equation (3)

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{K_a \times \text{Ch}}{C - \text{Ch}} = \frac{K_a \times h}{1 - h}$$

Since $h \ll \ll \ll 1$ then $(1 - h) \approx 1$

$$[\text{H}^+] = K_a \times h \quad [\text{Now put the value of } h \text{ from eq. (5)}]$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[\text{H}^+] = \sqrt{\frac{K_w \times K_a}{K_b}}} \quad \text{.....(8)}$$

$$\text{taking } -\log \text{ on both sides } -\log [\text{H}^+] = -\log \left(\frac{K_w \times K_a}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} [\log (K_w \times K_a) - \log K_b]$$

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$\text{pH} = -\frac{1}{2} [\log K_w] - \frac{1}{2} [\log K_a] - \frac{1}{2} [-\log K_b]$$

$$\text{pH} = +\frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

$$\boxed{\text{pH} = 7 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b} \quad \text{.....(9)}$$



GOLDEN KEY POINTS

- Degree of hydrolysis, pH of weak acid and weak base [WA – WB] type salts do not depend on the concentration of salt.

	SA SB salts	SA WB salts	WA SB salts	WA WB salts
1.	Neutral solution	Acidic solution	Basic solution	Almost neutral solution
2.	No hydrolysis	Cationic hydrolysis	Anionic hydrolysis	Hydrolysis by both cation and anion
3.	–	$K_h = \frac{K_w}{K_b}$	$K_h = \frac{K_w}{K_a}$	$K_h = \frac{K_w}{K_a \times K_b}$
4.	–	$h = \sqrt{\frac{K_w}{K_b \cdot C}}$	$h = \sqrt{\frac{K_w}{K_a \cdot C}}$	$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$
5.	–	$[H^+] = C \cdot h = \sqrt{\frac{K_w \cdot C}{K_b}}$	$[OH^-] = C \cdot h = \sqrt{\frac{K_w \cdot C}{K_a}}$	$[H^+] = K_a \cdot h = \sqrt{\frac{K_w \cdot K_a}{K_b}}$
6.	–	$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$	$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$	$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

Illustrations

Illustration 12 What is the pH of 1 M CH_3COONa solution? K_a of acetic acid = 1.8×10^{-5} , $K_w = 10^{-14} \text{ mol}^2 \text{ L}^{-2}$
 (1) 2.4 (2) 3.6 (3) 4.8 (4) 9.4

Solution **Ans. (4)**

Illustration 13 Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN
 If $K_a = 10^{-5}$ and $K_b = 10^{-5}$

Solution Salt is [WA – WB]

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}} = \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

Illustration 14 **Assertion :** An aqueous solution of NH_4NO_3 is acidic in characters.

Reason : NH_4NO_3 in an aqueous solution undergoes anionic hydrolysis.

(1) A (2) B (3) C (4) D

Solution **Ans. (3)**

BEGINNER'S BOX-2

- When sodium acetate (CH_3COONa) is added to aqueous solution of acetic acid (CH_3COOH), the–
 (1) the pH value becomes zero (2) pH value remains unchanged
 (3) pH value decreases (4) pH value increases
- Which of the following cations is not hydrolyzed in aqueous solution ?
 (i) Mg^{2+} (ii) Ca^{2+} (iii) Na^+ (iv) K^+
 (1) (i), (ii) (2) (iii), (iv) (3) (i), (ii), (iii), (iv) (4) (i), (ii), (iii)



3. Which of the anions is not hydrolyzed in aqueous solution ?
 (i) Cl^- (ii) NO_3^- (iii) Br^- (iv) ClO_4^-
 (1) (i), (ii), (iii), (iv) (2) (ii), (iii), (iv) (3) (i), (ii), (iii) (4) (ii), (iv)
4. Which of the following salts does not undergo hydrolysis ?
 (1) KCN (2) KCl (3) NH_4NO_3 (4) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
5. Which of the following salts undergoes anionic hydrolysis ?
 (1) AlCl_3 (2) CuSO_4 (3) Na_2CO_3 (4) NH_4Cl
6. For cationic hydrolysis, pH is given by—
 (1) $\text{pH} = \frac{1}{2}\text{pK}_w + \frac{1}{2}\text{pK}_a + \frac{1}{2}\log C$ (2) $\text{pH} = \frac{1}{2}\text{pK}_w - \frac{1}{2}\text{pK}_b - \frac{1}{2}\log C$
 (3) $\text{pH} = \frac{1}{2}\text{pK}_w + \frac{1}{2}\text{pK}_a - \frac{1}{2}\text{pK}_b$ (4) $\text{pH} = \frac{1}{2}\text{pK}_w + \frac{1}{2}\text{pK}_b + \frac{1}{2}\log C$
7. Which of the following salts is neutral in water ?
 (1) KCl (2) NH_4NO_3 (3) NH_4CN (4) NH_4OH

4.6 SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

(A) SOLUBILITY

- (a) **Definition** At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution (i.e. saturated solution) is called solubility.

$$S(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$S = \frac{x}{M_w \times V_L} \text{ mol L}^{-1}$$

$$S_{g/\ell} = S_M \times \text{molar mass}$$

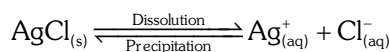
GOLDEN KEY POINTS

- Solubility does not depend on amount of substances and volume of solution where as depends on the following—
 (i) Temperature
 (ii) Presence of common ion
 (iii) Nature of solvent (Molecular wt. of $\text{AgCl} = 143.5$)
 (Molecular wt. of $\text{BaSO}_4 = 233$)
- Solubility can be expressed in terms of molarity.

(B) SOLUBILITY PRODUCT (K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.



according to law of mass action
$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$



Since, the concentration of undissolved solid AgCl is constant. Thus, the product $K.[AgCl]$ gives another constant which is designated as K_{sp} .

$$\text{So, } K.[AgCl] = [Ag^+].[Cl^-] \quad \therefore K_{sp} = [Ag^+] \cdot [Cl^-]$$

At constant temperature product of concentrations of ions in a saturated solution of substance is called solubility product of that substance. (Saturated solution is that solution in which solid solute and the ions in solution remain in equilibrium with each other.

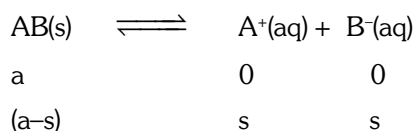
- **K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$
Solubility product in terms of concentration of ions $K_{sp} = [Ca^{+2}] [Cl^-]^2$
- **K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$
Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}] [Cl^-]^3$
- **General form** $A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$
 $K_{sp} = [A^{+y}]^x [B^{-x}]^y$

4.7 APPLICATION OF SOLUBILITY PRODUCT (K_{sp})

(A) To find out the solubility (S) :

(i) **K_{sp} of AB (Mono-mono, di-di, tri-tri valency) type salt -**

Ex. NaCl, $BaSO_4$, CH_3COONa , $CaCO_3$, NaCN, KCN, NH_4CN , NH_4Cl etc.

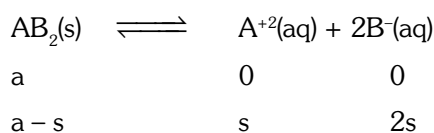


$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii) **K_{sp} of AB_2 or A_2B (Mono-di or di-mono valency) type salt -**

Ex. $CaCl_2$, $CaBr_2$, K_2S , $(NH_4)_2SO_4$, K_2SO_4 , K_2CO_3 etc.



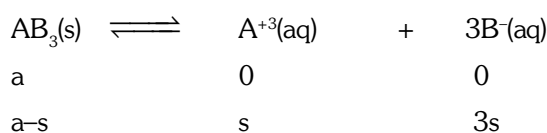
$$K_{sp} = [A^{+2}] [B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

(iii) **K_{sp} of AB_3 or A_3B (Mono-tri or tri-mono valency) type salt -**

Ex. $FeCl_3$, $AlCl_3$, K_3PO_4 etc.



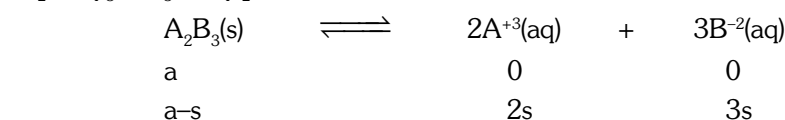
$$K_{sp} = [A^{+3}] [B^-]^3 = s \times (3s)^3 = 27s^4$$

$$s = \left(\frac{K_{sp}}{27} \right)^{\frac{1}{4}}$$



(iv) K_{sp} of A_2B_3 or A_3B_2 (Di-tri or tri-di valency) type salt

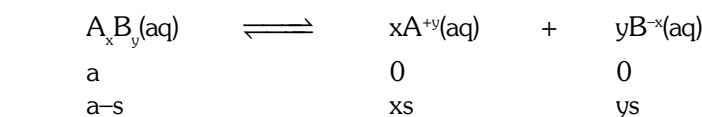
Ex. $Al_2(SO_4)_3$, $Ba_3(PO_4)_2$ etc.



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3 = 2s \times 2s \times 3s \times 3s \times 3s = 108s^5$$

$$s = \left(\frac{K_{sp}}{108} \right)^{1/5}$$

(v) General form :



$$K_{sp} = [A^{+y}]^x \cdot [B^{-x}]^y$$

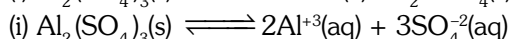
$$K_{sp} = (xs)^x \cdot (ys)^y \quad \boxed{K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}}$$

Illustrations

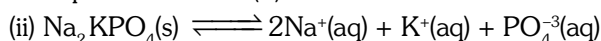
Illustration 15 What will be the solubility product of following in terms of solubility (mol L^{-1})

(i) $Al_2(SO_4)_3(s)$ (ii) $Na_2KPO_4(s)$ (iii) $NaKRbPO_4(s)$

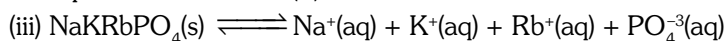
Solution



$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$



$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$



$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

Illustration 16 If solubility product of the base $M(OH)_3$ is 2.7×10^{-11} , the concentration of OH^{-1} will be
(1) 3×10^{-3} (2) 3×10^{-4} (3) 10^{-3} (4) 10^{-11}

Solution

Ans. (1)

Illustration 17 **Assertion :** For a sparingly soluble salt, S is the maximum dissolved value of solute in a solution.

Reason : K_{sp} corresponds to the ionic product of the salt in a saturated solution.

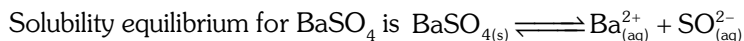
(1) A (2) B (3) C (4) D

Solution

Ans. (2)

Illustration 18 The solubility of $BaSO_4$ in water is $1.07 \times 10^{-5} \text{ mol dm}^{-3}$. Estimate its solubility product.

Solution



The solubility product is, $K_{sp} = [Ba^{2+}] [SO_4^{2-}]$

If S is the molar solubility of $BaSO_4$, then $K_{sp} = S^2$ because $x = 1 = y$.

Now, $S = 1.07 \times 10^{-5} \text{ M}$.

$$\text{Hence, } K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$$

Illustration 19 The solubility product of $AgBr$ is 5.2×10^{-13} . Calculate its solubility in mol dm^{-3} and g dm^{-3} . (Molar mass of $AgBr$ = 187.8 g mol^{-1})

Solution



and $K_{sp} = [Ag^+] [Br^-] = S^2$ because $x = 1 = y$.

$$\text{The molar solubility } S \text{ of } AgBr \text{ is given by } S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in g dm^{-3} = molar solubility (mol dm^{-3}) \times molar mass (g mol^{-1})

$$\text{Hence, solubility} = 7.2 \times 10^{-7} (\text{mol dm}^{-3}) \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}.$$



(B) Condition of precipitation /Ionic product (IP or Q_{sp}) :

- Ionic product (IP) of an electrolyte is defined in the same way as K_{sp} . The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.
 $Q_{sp} = IP = [Ag^+]_i [Cl^-]_i$ and $K_{sp} = [Ag^+]_{eq} [Cl^-]_{eq}$
- Ionic product changes with concentration but K_{sp} does not. K_{sp} is applicable for saturated solution of the sparingly soluble electrolyte.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :
 - $Q_{sp} < K_{sp}$: The solution is unsaturated and precipitation will not occur.
 - $Q_{sp} = K_{sp}$: The solution is saturated and solubility equilibrium exists.
 - $Q_{sp} > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

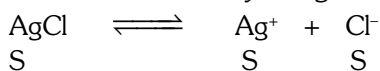
(C) Common ion effect on solubility :

Important point :- Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established so, the solubility of substances decreases but K_{sp} remains same because it is an equilibrium constant which depends only on temperature.

Illustrations

Illustration 20 Find out the solubility of AgCl in the presence of C molar NaCl solution ?

Solution.

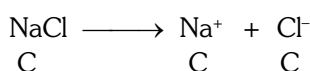


(Let solubility of AgCl is S mol L⁻¹)

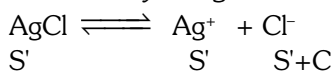
$$K_{sp} = [Ag^+] [Cl^-]$$

$$K_{sp} = S^2$$

In NaCl solution



Let solubility of AgCl in the presence of NaCl solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [Ag^+] [Cl^-]$$

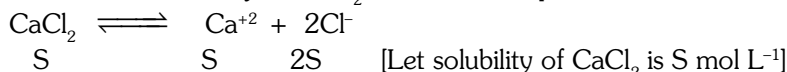
$$K_{sp} = S' (S' + C) = S'^2 + S'C \quad (\text{Neglecting the higher power terms of } S')$$

$$K_{sp} = S' C$$

$$S' = \frac{K_{sp}}{C}$$

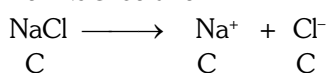
Illustration 21 Find out the solubility of CaCl₂ solution in the presence of C NaCl solution ?

Solution

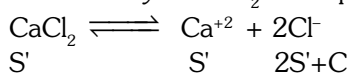


$$K_{sp} = [Ca^{+2}] [Cl^-]^2 = 4S^3$$

For NaCl solution



Let solubility of CaCl₂ in the presence of NaCl solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [Ca^{+2}] [Cl^-]^2$$

$$K_{sp} = S' (2S' + C)^2 = S' (4S'^2 + 4S'C + C^2)$$

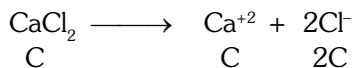
$$K_{sp} = 4S'^3 + 4S'^2 C + S' C^2 \quad (\text{Neglecting the higher power terms of } S')$$

$$S' = \frac{K_{sp}}{C^2}$$

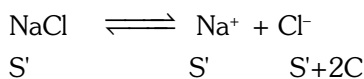


Illustration 22 Find out the solubility of NaCl in the presence of C CaCl₂ solution ?

Solution



Let solubility of NaCl in the presence of CaCl₂ solution is S' mol L⁻¹.



According to L.M.A.

$$K_{sp} = [\text{Na}^+][\text{Cl}^-]$$

$$K_{sp} = S' (S' + 2C) = S'^2 + 2S'C \text{ (Neglecting the higher power terms of S')}$$

$$S' = \frac{K_{sp}}{2C}$$

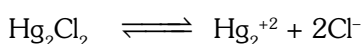
GOLDEN KEY POINTS

● **Group precipitation of Salt**

Group	Radicals	Condition for precipitation (Group reagent)	Forms of precipitation
Zero	NH ₄ ⁺
First	Pb ⁺² , Hg ⁺¹ , (Hg ₂ ⁺²), Ag ⁺	By mixing of dilute HCl	Chloride AgCl, Hg ₂ Cl ₂ , PbCl ₂
Second II(A)	Pb ⁺² , Cu ⁺² , Hg ⁺² , Cd ⁺² , Bi ⁺³	H ₂ S gas passed in	Sulphide
Second II(B)	As ⁺³ , Sb ⁺³ , Sn ⁺² , Sn ⁺⁴	the presence of acidic medium	PbS, HgS, CuS, CdS, SnS, SnS ₂ , As ₂ S ₃ , Sb ₂ S ₃ , Bi ₂ S ₃
Third	Al ⁺³ , Cr ⁺³ , Fe ⁺³	NH ₄ OH mixed in the presence of NH ₄ Cl	Hydroxide Al(OH) ₃ , Fe(OH) ₃ , Cr(OH) ₃
Fourth	Zn ⁺² , Ni ⁺² , Mn ⁺² , Co ⁺²	H ₂ S gas passed in presence of basic medium	Sulphide MnS, CoS, NiS, ZnS
Fifth	Ba ⁺² , Sr ⁺² , Ca ⁺²	(NH ₄) ₂ CO ₃ mixed in the presence of NH ₄ Cl	Corbonate BaCO ₃ , SrCO ₃ , CaCO ₃
Sixth	Na ⁺ , K ⁺ , Mg ⁺²	By mixing of Na ₂ HPO ₄	Hydrogen phosphate (MgHPO ₄)

● Hg⁺¹(us) → Unstable in aqueous solution.

[Stable in dimer form (Hg₂⁺²) ⇒ Hg₂Cl₂]



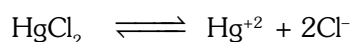
$$S \qquad S \qquad 2S$$

$$K_{sp} = [\text{Hg}_2^{+2}][\text{Cl}^-]^2$$

$$= (S)(2S)^2$$

$$K_{sp} = 4S^3$$

● Hg⁺²(ic) → HgCl₂ → stable in aqueous solution



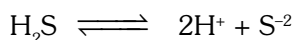
$$S \qquad S \qquad 2S$$

$$K_{sp} = 4S^3$$



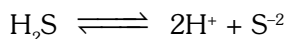
- For precipitation of II group, H_2S gas is passed in acidic medium to decrease S^{2-} concentration by common ion effect. So that ionic product of cations of group II and S^{2-} ions exceed the solubility product of their corresponding metal sulphides. Therefore only the cations of group II gets precipitated. But the sulphides of the cation of the other groups (III, IV & V) are not precipitated under these conditions because their solubility products are quite high.

When H_2S gas is directly passed through solution then IVth group is also precipitated with IInd group.



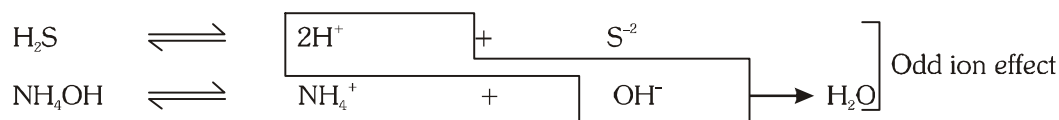
$$K_{sp_{II}} < K_{sp_{IV}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}]$$

When H_2S gas pass in acidic medium $[\text{H}^+]$ then only IInd group radicals are precipitated.



$$K_{sp_{II}} < [\text{radicals of II}^{\text{nd}} \text{ and IV group}] [\text{S}^{2-}] < K_{sp_{IV}}$$

- For precipitation of group III, NH_4OH is added in the presence of NH_4Cl to decrease the concentration of OH^- by common ion effect so that ionic product of cations of group III and hydroxides ions exceed the solubility product of their corresponding metal hydroxides and only group III cations will precipitated. On the other hand cations of group IV, V and VI, which require large concentration of OH^- due to their high solubility product, will not be precipitated.
- In IV group, H_2S gas is passed in basic medium to increase S^{2-} ion concentration by odd ion effect, so that the ionic product of cations of group IV and S^{2-} ions exceed the solubility product of their corresponding metal sulphide and hence gets precipitated.



So $[\text{S}^{2-}] \uparrow$

$$K_{sp_{IV}} < [\text{Radicals of group IV}] [\text{S}^{2-}]$$

(D) Precipitation of soap and salt (NaCl)

(i) Precipitation of NaCl (common salt) :

For the precipitation of NaCl, HCl gas passed in saturated solution of NaCl to increase the concentration of Cl^- ion by common ion, so ionic product of concentration of Na^+ and Cl^- ion becomes more than K_{sp} of NaCl and NaCl easily precipitated.



$$K_{sp} = [\text{Na}^+] [\text{Cl}^-]$$



due to common ion $K_{sp} < [\text{Na}^+] [\text{Cl}^-] \uparrow$

(ii) Precipitation of soap :

For precipitation of soap, NaCl mixed in saturated solution of soap to increase the concentration of Na^+ ion by common ion. So ionic product of concentration of Na^+ and stearate ions is more than K_{sp} of soap and soap is easily precipitated.

Ex. $\text{C}_{17}\text{H}_{35}\text{COONa}$ (Sodium stearate)



$$K_{sp} = [\text{C}_{17}\text{H}_{35}\text{COO}^-] [\text{Na}^+]$$



due to common ion $K_{sp} < [\text{C}_{17}\text{H}_{35}\text{COO}^-] [\text{Na}^+] \uparrow$



Illustrations

Illustration 23 Solubility products of $M(OH)_3$ and $M(OH)_2$ are 10^{-23} and 10^{-14} respectively. Which will be precipitated first on adding NH_4OH , if M^{+2} and M^{+3} both the ions are in solution ?

(1) M^{+2}

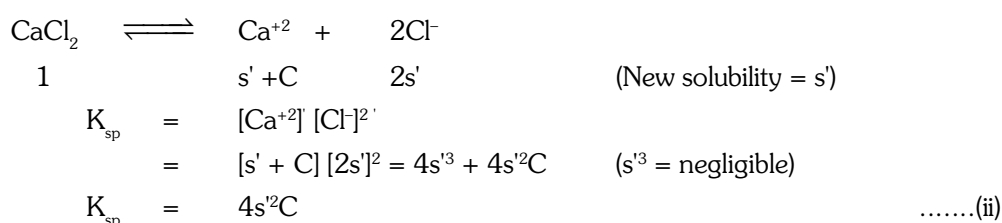
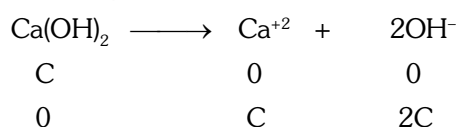
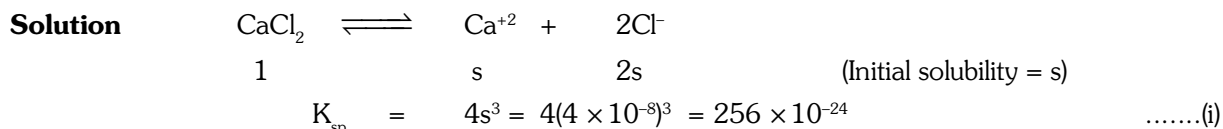
(2) M^{+3}

(3) Both M^{+2} and M^{+3} together

(4) Precipitation will not take place.

Solution **Ans. (2)**

Illustration 24 Solubility of $CaCl_2$ is 4×10^{-8} , then find out its K_{sp} and its new solubility in the presence of 10^{-2} M $Ca(OH)_2$.



From equation (i) and (ii) $s'^2 = \frac{K_{sp}}{4C} = \frac{256 \times 10^{-24}}{4 \times 10^{-2}} = 64 \times 10^{-22}$

$s' = 8 \times 10^{-11} \text{ mol L}^{-1}$

4.8 FEW IMPORTANT POINTS

(A) Isohydric solution – If different-different solution has same pH are called isohydric solution.

Sp. point :- Isohydric conditions for two given weak acids HA_1 and HA_2 which has concentration C_1 and C_2 and ionisation constants are K_{a1} and K_{a2} respectively.

$$\text{Then } [H^+]_1 = \sqrt{K_{a1} C_1} \text{ and } [H^+]_2 = \sqrt{K_{a2} C_2}$$

According to given condition for isohydric solution pH of different solution is same.

Hence $[H^+]_1 = [H^+]_2$

$$\sqrt{K_{a1} C_1} = \sqrt{K_{a2} C_2}$$

$$\boxed{K_{a1} C_1 = K_{a2} C_2} \text{ or If } n = 1 \text{ mole then } \boxed{\frac{K_{a1}}{V_1} = \frac{K_{a2}}{V_2}} \therefore \boxed{C \propto \frac{1}{V}}$$

(B) Relative strength of Acids :- It indicates that how many times an acid is stronger than the other acid.

We know $\boxed{\text{Strength of acid} \propto [H^+]}$

If there are two weak acids HA_1 and HA_2 which has concentration C_1 and C_2 , degree of ionisation α_1 and α_2 and ionisation constants K_{a1} and K_{a2} respectively then ratio of their strength of acids.

We know $[H^+] = C\alpha = \sqrt{K_a C}$

$$\text{So } \frac{\text{Strength of weak acid } HA_1}{\text{Strength of weak acid } HA_2} = \frac{[H^+]_1}{[H^+]_2} = \frac{C_1 \alpha_1}{C_2 \alpha_2} = \frac{\sqrt{K_{a1} C_1}}{\sqrt{K_{a2} C_2}}$$



If $C_1 = C_2$

$$\text{R.S.} = \frac{\text{Strength of weak acid HA}_1}{\text{Strength of weak acid HA}_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \frac{\alpha_1}{\alpha_2}$$

Thus the relative strength of two acids of equimolar concentration can be compared by taking square root of the ratio of their ionisation constants.

Illustrations

Illustration 25 Which of the following solvents will undergo self-ionization ?

- (1) H_2O (2) NH_3 (3) HF (4) All of these

Solution **Ans. (4)**

Illustration 26 For two acids A and B, $\text{p}K_{a1} = 1.2$, $\text{p}K_{a2} = 2.8$ respectively in value, then which is true:-

- (1) A & B both are equally acidic
(2) A is stronger than B
(3) B is stronger than A
(4) None of these

Solution **Ans. (2)**

Illustration 27 pH values of two acids A and B are 4 and 5. The strengths of these two acids are related as :-

- (1) The strengths of the two acids cannot be compared.
(2) Acid B is 10 times stronger than acid A.
(3) Strength of acid A : Strength of acid B = 4 : 5
(4) Acid A is 10 times stronger than acid B.

Solution **Ans. (4)**

BEGINNER'S BOX-3

- The units of solubility product of silver chromate (Ag_2CrO_4) will be-
(1) $\text{mol}^2\text{L}^{-2}$ (2) $\text{mol}^3\text{L}^{-3}$ (3) mol L^{-1} (4) mol^{-1}L
- At a certain temperature, the solubility of the salt A_xB_y is S moles per liter. The general expression for its solubility product will be-
(1) $K_{sp} = x^y y^x S^{x+y}$ (2) $K_{sp} = (xy)^{x+y} S^{x+y}$ (3) $K_{sp} = (x^x y^y) S^{x+y}$ (4) $K_{sp} = x^x y^y S^{xy}$
- The molar solubility of silver sulphate is $1.5 \times 10^{-2} \text{ mol L}^{-1}$. The solubility product of the salt will be-
(1) 2.25×10^{-4} (2) 1.35×10^{-5} (3) 1.7×10^{-6} (4) 3.0×10^{-3}
- The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed:
(1) $10^{-3} \text{ M Ca}^{2+} + 10^{-5} \text{ M F}^-$ (2) $10^{-5} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$
(3) $10^{-2} \text{ M Ca}^{2+} + 10^{-3} \text{ M F}^-$ (4) $10^{-4} \text{ M Ca}^{2+} + 10^{-4} \text{ M F}^-$
- If S_0 , S_1 , S_2 and S_3 are the solubilities of AgCl in water, 0.01 M CaCl_2 , 0.01 M NaCl and 0.5 M AgNO_3 solutions, respectively, then which of the following is true?
(1) $S_0 > S_2 > S_1 > S_3$ (2) $S_0 = S_2 = S_1 > S_3$
(3) $S_3 > S_1 > S_2 > S_0$ (4) $S_0 > S_2 > S_3 > S_1$
- Given $K_{sp}(\text{AgI}) = 8.5 \times 10^{-17}$. The solubility of AgI in 0.1 M KI solution is-
(1) 0.1 M (2) $8.5 \times 10^{-16} \text{ M}$
(3) $8.5 \times 10^{-17} \text{ M}$ (4) $8.5 \times 10^{-18} \text{ M}$



4.9 pH

1. INTRODUCTION

pH of some important substance :-

(i)	Blood	→	7.4
(ii)	Tear	→	7.4
(iii)	Gastric Juice	→	1 to 3
(iv)	Soft drink	→	2 to 4
(v)	Acidic rain	→	6
(vi)	Milk	→	6.3 to 6.6
(vii)	Water	→	7

2. TYPES OF pH

- (i) pH of SA and SB. $[H^+] = C$, $[OH^-] = C$
- (ii) pH of WA and WB. $[H^+] = C\alpha$, $[OH^-] = C\alpha$
- (iii) pH of very dilute solution. (Consider H^+ & OH^- of H_2O also)
- (iv) pH of salt solution.
 - (a) SA SB Type Salt (always 7)
 - (b) SA WB Type Salt (< 7)
 - (c) WA SB Type Salt (> 7)
 - (d) WA WB Type Salt (Almost 7)

3. pH of mixture of acid and base.

- (a) pH of mixture of strong acids :

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$$

$$V = \text{Volume of final solution} = V_1 + V_2 + V_3 + \dots$$

$$N = \text{Normality of final solution} = [H^+] \text{ in final solution.}$$

- (b) pH of mixture of strong base :

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = NV$$

$$V = \text{Volume of final solution} = V_1 + V_2 + V_3 + \dots$$

$$N = \text{Normality of final solution} = [OH^-] \text{ in final solution.}$$

- (c) pH of mixture of strong acids and strong bases :

For acid :

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{\text{Acid}}$$

For base :

$$N_1V_1 + N_2V_2 + N_3V_3 + \dots = (NV)_{\text{Base}}$$

- (i) If $(NV)_{\text{Acid}} > (NV)_{\text{Base}}$ then solution is acidic.

$$NV = (NV)_{\text{Acid}} - (NV)_{\text{Base}} \quad \text{and}$$

$$[H^+] = N$$

- (ii) If $(NV)_{\text{Base}} > (NV)_{\text{Acid}}$ then solution is basic.

$$NV = (NV)_{\text{Base}} - (NV)_{\text{Acid}} \quad \text{and}$$

$$[OH^-] = N$$

- (iii) If, $(NV)_{\text{acid}} = (NV)_{\text{base}}$ then solution is neutral.

- (d) pH of mixture of (WA + SB); when equivalent of WA > SB]

pH of mixture of (SA + WB); When equivalent of WB > SA]



gives rise to concept of buffer solution



4.10 BUFFER SOLUTION

(A) **Definition** : A solution which resist the change in pH and pH does not change significantly on addition of small amount of strong acid or strong base is called buffer solution.

(B) **Properties of buffer solution** :

- (i) The pH of buffer solution does not change appreciably upon the addition of small amount of either strong acid or strong base.
- (ii) The pH of buffer solution does not depend on the volume of solution. Hence, solution can be diluted without change in pH.
- (iii) The pH of buffer solution remains constant even if it is kept for a long time.

(C) **Buffer solutions are used in**

- (a) Qualitative analysis of mixture
- (b) Quantitative analysis of mixture
- (c) Digestion of food
- (d) Preservation of food and fruits.
- (e) Agriculture and dairy product preservation.
- (f) Industrial process such as manufacture of paper, dyes inks, paints, drugs etc.

TYPES OF BUFFER SOLUTION

(A). Simple buffer solution

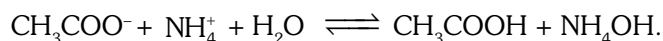
(B). Mixed buffer solution :- (i) Acidic buffer solution (ii) Basic buffer solution

(A) **Simple buffer solution :-** Aqueous solution of weak acid-weak base (WA – WB) types of salt.

Ex. $\text{CH}_3\text{COONH}_4$, NH_4CN , AgCN etc.

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$$

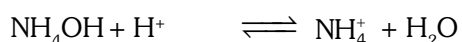
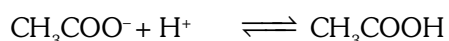
pH does not depend on concentration.



Buffer Action :

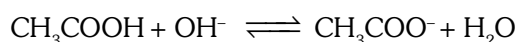
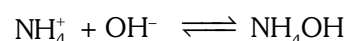
Case 1

When mixing of acid $[\text{H}^+]$



Case 2.

When mixing of base $[\text{OH}^-]$

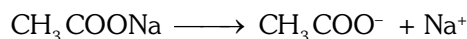
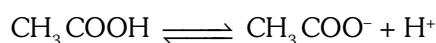
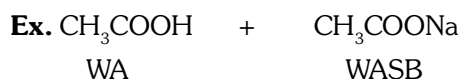


(B) **Mixed buffer solution** :

(i) **Acidic buffer solution :-** The solution in which weak acid and its conjugate base are present.

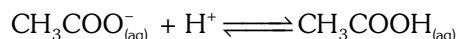
OR

Aqueous solution of mixture of weak acid and salt of same weak acid with any strong base is called acidic buffer solution.

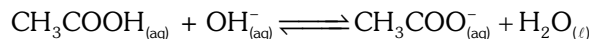


BUFFER ACTION :-

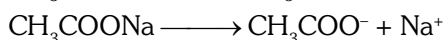
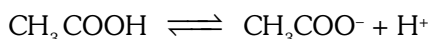
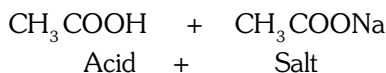
Case 1. If a small amount of acid is added to the buffer solution. The H^+ ions of the acid react with CH_3COO^- ions and produce CH_3COOH and most of the added H^+ ions are consumed so there is no appreciable change in pH.



Case 2. If small amount of base is added to the buffer solution, the OH^- ions are consumed by CH_3COOH .



So, there is no appreciable change in pH.

(a) pH of acidic buffer solution :

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$\text{or } [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a[\text{Acid}]}{[\text{Conjugate base}]}$$

taking $-\log$ on both sides

$$pH = pK_a - \log \frac{[\text{Acid}]}{[\text{Conjugate base}]} \quad \text{or} \quad pH = pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Henderson's equation :

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{or} \quad \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

- $[\text{Conjugate base}]_{eq} \approx [\text{Salt}]$ because CH_3COO^- mainly comes from salt since dissociation of CH_3COOH in presence of CH_3COONa is appreciably decreased.
- $[\text{Acid}]_{aq} \approx$ initial concentration of acid since it is almost unionised in presence of salt due to common ion effect.

(b) pH range of acidic buffer solution : It depends on pK_a of acid and ratio of salt to acid concentrations.

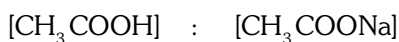
$$[CH_3COOH] : [CH_3COONa] \Rightarrow pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$(i) \quad \text{If, } 1 : 10 \Rightarrow pH = pK_a + \log \frac{10}{1} = pK_a + 1$$

$$(ii) \quad \text{If, } 10 : 1 \Rightarrow pH = pK_a - 1$$

So pH range

$$pH = pK_a \pm 1$$

(c) Maximum buffer action condition of acidic buffer solution :

$$1 : 1 \Rightarrow pH = pK_a + \log \frac{1}{1}$$

$$pH = pK_a$$

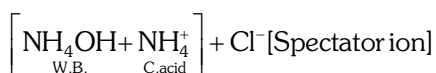
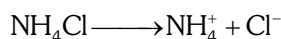
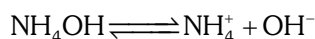


(ii) Basic buffer solution :

Definition : The solution in which weak base and its conjugate acid are present. OR

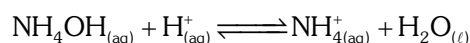
Aqueous solution of mixture of weak base and salt of same weak base with any strong acid is called basic buffer solution.

Ex. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$



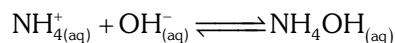
BUFFER ACTION :-

Case 1. If a small amount of the acid is added to the buffer solution, the H^+ ions are consumed by NH_4OH .



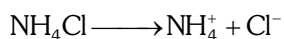
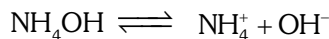
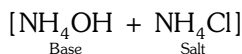
So there is no appreciable change in pH.

Case 2. If small amount of base is added to the buffer solution, the OH^- ions react with NH_4^+ ions to produce NH_4OH .



Hence most of the added OH^- ions are consumed. so there is no appreciable change in pH.

(a) pOH of basic buffer solution :



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \text{or} \quad [\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

taking $-\log$ on both sides $\quad \text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$

Henderson's equation :

$$\boxed{\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \text{ or } \frac{[\text{Conjugate acid}]}{[\text{Base}]}}$$

(b) pOH range of basic buffer solution : It depends on $\text{p}K_b$ of base and ratio of salt to base concentrations.

$$[\text{NH}_4\text{OH}] : [\text{NH}_4\text{Cl}] \Rightarrow \text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]}$$

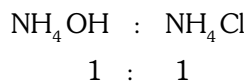
(i) If, 1 : 10 $\Rightarrow \text{pOH} = \text{p}K_b + 1$

(ii) If, 10 : 1 $\Rightarrow \text{pOH} = \text{p}K_b - 1$

So, pOH range : $\boxed{\text{pOH} = \text{p}K_b \pm 1}$



(c) **Maximum buffer action condition of basic buffer solution :**



$$\boxed{\text{pOH} = \text{pK}_b}$$

3. BUFFER CAPACITY

Definition :-

- (i) It is defined as the number of moles of strong acid (or strong base) added to one litre of a buffer solution to change its pH by one unit.
- (ii) It measures the effectiveness of a buffer.
- (iii) Larger the value of buffer capacity more resistant is the solution to pH change.

$$\text{Buffer capacity} = \frac{\text{Number of moles of acid or base added per litre}}{\text{Change in pH of buffer solution}}$$

Illustrations

Illustration 28 When 2 moles of HCl is added to 1 L. of an acidic buffer solution, its pH changes from 3.9 to 3.4. Find its buffer capacity.

Solution $\text{B.C.} = \frac{2}{0.5} = 4$

BEGINNER'S BOX-4

1. A buffer solution is one which has—
(1) reserved acid (2) reserved base (3) constant pH (4) pH equal to 7
2. Which of the following solutions cannot act as a buffer system ?
(1) $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ (2) $\text{NaClO}_4/\text{HClO}_4$ (3) $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{N}^+\text{HCl}^-$ (4) $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$
3. A buffer solution can not be prepared by mixing equimolar amounts of—
(1) B(OH)_3 and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (2) NH_3 and NH_4Cl
(3) HCl and NaCl (4) CH_3COOH and CH_3COONa
4. Which of the following salt solution will act as a buffer ?
(1) $\text{CH}_3\text{COONH}_4$ (aq.) (2) NH_4Cl (aq.) (3) CH_3COONa (aq.) (4) NaCl (aq.)
5. Which of the following combinations will make a buffer solutions ?
(i) CH_3COONa (2 mol) + HCl (1 mol) (ii) CH_3COOH (2 mol) + NaOH (1 mol)
(iii) CH_3COOH (1 mol) + CH_3COONa (1 mol)
(1) (iii) (2) (i), (ii) (3) (ii), (iii) (4) (i), (ii), (iii)
6. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system—
(1) $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (2) $\text{NH}_4\text{Cl}/\text{NH}_3$
(3) $\text{H}_2\text{PO}_4^{2-}$ (4) $\text{H}_2\text{CO}_3/\text{HCO}_3^-$



4.11 INDICATOR

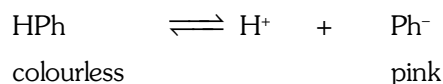
(A) **Definition :-** An indicator is a substance that undergoes change in its colour to show end point of an acid-base titration.

- Titration involves neutralization of an acid and base.

(B) **Types of indicators :**

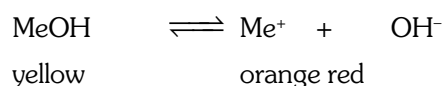
(a) **Acidic indicator (HIn)**

Ex. Phenolphthalein (HPh)



(b) **Basic indicator (InOH)**

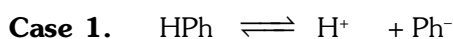
Ex. Methyl orange (MeOH)



OSTWALD THEORY OF INDICATORS

- According to this theory, all the indicators are weak organic acid or base.
- Every indicator has light colour in its unionised form and dark colour in ionised form.
- Every indicator has one colour in acidic medium and an altogether different colour in basic medium due to common ion effect and odd ion effect.

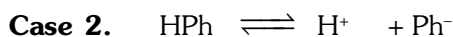
Ex. Acidic indicator [HPh]



In acidic medium $[\text{H}^+]$

$$[\text{HPh}] > [\text{Ph}^-]$$

Colourless due to common ion effect.

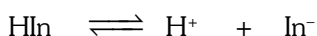


In basic medium $[\text{OH}^-]$

$$[\text{Ph}^-] > [\text{HPh}]$$

Pink colour due to odd ion effect.

(a) **pH of acidic indicator -**



$$K_a \text{ or } K_i = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}^+] = \frac{K_i [\text{HIn}]}{[\text{In}^-]}$$

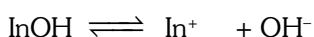
Taking - log on both sides

$$\text{pH} = \text{p}K_i - \log [\text{HIn}] + \log [\text{In}^-]$$

$$\text{pH} = \text{p}K_i + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\boxed{\text{pH} = \text{p}K_i + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$

(b) **pOH of basic indicator -**



$$K_b \text{ or } K_i = \frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]}$$

$$\boxed{\text{pOH} = \text{p}K_i + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}}$$



(c) pH range of indicators :

Indicators show colour change for a certain pH range not at a definite pH which is called pH range of indicator.

(i) pH range of acidic indicator :

$$\begin{array}{ccc} [\text{HIn}] & : & [\text{In}^-] \\ 1 & : & 10 \\ 10 & : & 1 \end{array} \quad \boxed{\text{pH} = \text{pK}_i \pm 1}$$

(ii) pOH range of basic indicator :

$$\begin{array}{ccc} [\text{InOH}] & : & [\text{In}^+] \\ 1 & : & 10 \\ 10 & : & 1 \end{array} \quad \boxed{\text{pOH} = \text{pK}_i \pm 1}$$

(iii) Neutral condition for indicators (No working condition)

For acidic indicator

$$\begin{array}{ccc} [\text{HIn}] & : & [\text{In}^-] \\ 1 & : & 1 \end{array}$$

$$\boxed{\text{pH} = \text{pK}_i}$$

For basic indicators

$$\begin{array}{ccc} [\text{InOH}] & : & [\text{In}^+] \\ 1 & : & 1 \end{array}$$

$$\boxed{\text{pOH} = \text{pK}_i}$$

S.No.	Name of indicator	Colour in acidic medium	Colour in basic medium	Working pH range of indicators
1.	Methyl orange (MeOH)	Orange red	Yellow	3.1 to 4.5
2.	Methyl red	Red	Yellow	4.2 to 6.2
3.	Phenol red	Yellow	Red	6.2 to 8.2
4.	Phenolphthalein (HPh)	Colourless	Pink	8.2 to 10.2

3. ACID-BASE TITRATION

S.No.	Type of titration	pH range of titration	Suitable indicators
1.	SA/SB.	3 – 11	All indicators (MeOH, HPh etc.)
2.	SA/WB	3 – 7	Methyl orange (MeOH) and methyl red
3.	WA/SB	7 – 11	Phenolphthalein (HPh)

Important points of titration :

- Titration is always possible in two opposite solution. (i.e. one is acidic and other is basic).
- For any titration only that indicator is suitable if their working pH range is in pH range of titration.
- At the end point of titration equivalents of acids and bases are always same.
- At the equivalence point, nature of solution depends on the type of titration.

- SA/SB - Neutral (pH = 7)
SA/WB - Acidic
WA/SB - Basic
WA/WB - Any one possible



4.12 ACID AND BASE

(1) INTRODUCTION

The earliest classification of substances into acids and bases was based upon the characteristic properties possessed by each one of them. For example,

Acid was defined as a substance whose aqueous solution possesses the following characteristic properties:

- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns blue litmus red.
- (iv) has a sour taste.
- (v) whose acidic properties disappear on reaction with a base.

Base was defined as a substance whose aqueous solution possessed the following characteristic properties:

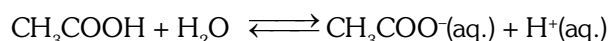
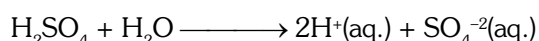
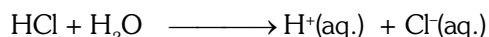
- (i) conducts electricity,
- (ii) reacts with active metals like zinc, magnesium etc. to give hydrogen,
- (iii) turns red litmus blue,
- (iv) has a bitter taste
- (v) whose basic properties are destroyed on reaction with an acid.

The above definitions of acids and bases are called operational definitions as they are based on certain operations (i.e. tests) to be performed on the substances. However, these have been replaced by conceptual definitions (put forward by Arrhenius, Bronsted-Lowry and Lewis) which go into the causes of the observed behavior, based upon structure and composition of the substances.

(2) Arrhenius Concept (1884)

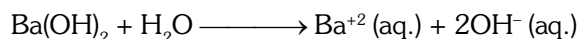
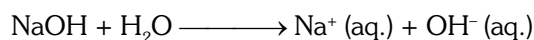
(a) Acid:- According to this concept, those substances which produce free H^+ ions in aqueous solution are called acid.

Example $HCl, HNO_3, H_2SO_4, H_3PO_4, H_2CO_3, H_2S, CH_3COOH$ etc.



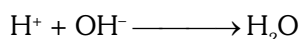
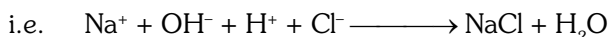
(b) Base :- Those substances which produce free OH^- ions in aqueous solution are called base.

Example $NaOH, KOH, CsOH, RbOH, NH_4OH, Ba(OH)_2, Ca(OH)_2, Al(OH)_3$ etc.



(c) Nature of water :- According to this concept nature of water is neutral and act as a solvent.

(d) Neutralisation Reaction :- Those reactions in which acid and base react together to form water molecule are called neutralisation reactions.



(e) Strength of acids and bases :- This concept explains the strength of acids and bases depending upon the basis of degree of ionisation.

Example For strong electrolytes $\alpha \simeq 100\%$

For weak electrolytes $\alpha < 100\%$

(f) Advantage :- This concept explains the acids and bases practically. i.e. To find out the pH, ionisation constant, hydrolysis constants, heat of neutralisation etc.



(g) Disadvantage :-

It explains the behaviour of acids and bases only in aqueous (water) solvents.

Illustrations

Illustration 29 Gaseous hydrogen chloride is a very poor conductor of electricity but a solution of hydrogen chloride in water is a good conductor. This is due to the fact that :-

- (1) Water is a good conductor of electricity
- (2) Hydrogen chloride ionises in water
- (3) A gas cannot conduct electricity but a liquid can
- (4) HCl does not obey Ohm's law whereas the solution does

Solution (2)

Illustration 30 Which is acid in the following pairs according to Arrhenius concept ?

- (1) HCl(g) and HCl(aq) (2) $\text{CH}_3\text{COOH(l)}$ and $\text{CH}_3\text{COOH(aq)}$

Solution (1) HCl(aq.) (2) $\text{CH}_3\text{COOH(aq.)}$

(3) Bronsted-Lowry Concept (1923)

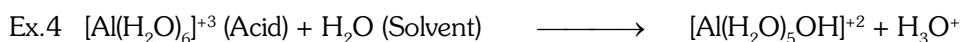
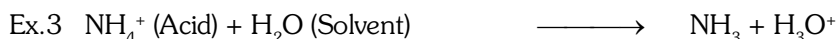
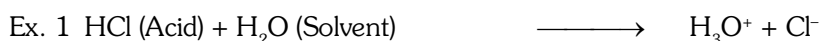
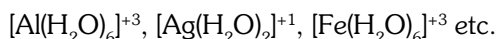
It is based upon the exchange of proton.

(a) Acid :- According to this concept those substances which have tendency to donate the proton (H^+) by any method in any solvent are called acids.

Example (i) Neutral molecules - HCl , HNO_3 , H_2SO_4 , H_2CO_3 , H_2S , CH_3COOH , H_3PO_3 etc.

(ii) Anions - HS^- , HCO_3^- , HSO_4^- , H_2PO_4^- , HPO_4^{2-} , H_2O etc.

(iii) Cations - NH_4^+ , H_3O^+ , PH_4^+ , $\text{CH}_3\text{COOH}_2^+$ etc.



(b) Base :- Those substances which have tendency to accept the proton by any method in any solvent are called the bases.

- (1) HS^- , HCO_3^- , HSO_4^- , H_2PO_4^- , HPO_4^{2-} , O^{2-} , SO_4^{2-} , CO_3^{2-} , Cl^- , Br^- , I^- , CN^- etc.
- (2) NH_3 , RNH_2 , R_2NH , R_3N , $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_5\text{H}_5\text{N}$, $\text{H}_2\text{N-NH}_2$ etc.

Example

- (i) $\text{HS}^- (\text{Base}) + \text{H}_2\text{O} (\text{Solvent}) \longrightarrow \text{H}_2\text{S} + \text{OH}^-$
- (ii) $\text{NH}_3 (\text{Base}) + \text{H}_2\text{O} (\text{Solvent}) \longrightarrow \text{NH}_4^+ + \text{OH}^-$
- (iii) $\text{CO}_3^{2-} (\text{Base}) + \text{H}_2\text{O} (\text{Solvent}) \longrightarrow \text{HCO}_3^- + \text{OH}^-$



GOLDEN KEY POINTS

Types of Solvent

(a) Protogenic or acidic solvent :- They have a tendency to generate or donate the protons.

Example CH_3COOH , HCl , HNO_3 , H_2SO_4 etc.

(b) Protophilic or basic solvent :- They have a tendency to accept the protons.

Example NH_3 , CH_3OH , RNH_2 etc.

(c) Amphotropic or amphoteric solvents :- They have the tendency to accept or donate the protons or they are either protophilic or proto-genic.

Example H_2O , HS^- , HSO_4^- , HCO_3^- etc.

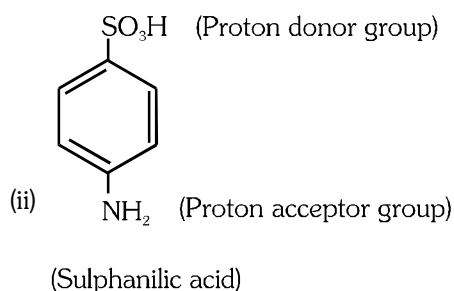
(d) Aprotic solvents :- They neither donate nor accept the protons.

Example C_6H_6 , CCl_4 , CHCl_3 , BrF_3 , NO_2 , COCl_2 etc.

(e) **Ampholyte solvents**-Those solvents in which the same molecule acts as proton donor and proton acceptor.

Example (i)
$$\text{H}_2\text{N}-\text{CH}_2-\text{COOH} \longrightarrow \text{H}_3^+\text{N}-\text{CH}_2-\text{COO}^-$$

(Glycine) (Zwitter ion)



(f) Advantage :-

- (i) It explain the behaviour of acids and bases in any type of solvent.
- (ii) It explain the stability of proton (H^+).

(g) Disadvantage :-

- (i) It does not explain the acid and base practically.
- (ii) It does not explain acidic behaviour of aprotic acid. (SO_2 , SO_3 , CO_2 , AlCl_3 , SiCl_4 etc.)

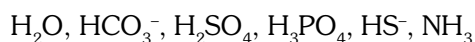
Illustrations

Illustration 31 In the process : $\text{NH}_3 + \text{NH}_3 \rightleftharpoons \text{NH}_2^- + \text{NH}_4^+$, The nature of ammonia is:-

- (1) Acidic (2) Basic (3) Amphoteric (4) None

Solution. **Ans.(3)**

Illustration 32 Which of the following behave both as Bronsted acid as well as Bronsted bases ?

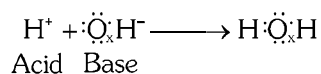


Solution. H_2O , HCO_3^- , HS^- , NH_3



(4) Lewis Concept (1939)

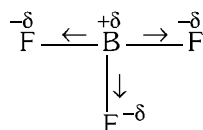
(a) **Lewis Acid :-** According to this concept those species which have self tendency to accept the lone pair of electrons are called acids. i.e. Lewis acid is an electron pair acceptor (electrophilic).



Classification of Lewis Acids :-

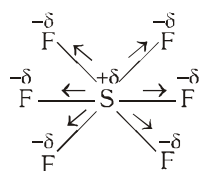
(i) Compounds whose central atom have an incomplete octet (electron deficient)

Example BF_3 , BBr_3 , BCl_3 , BI_3 , $\text{B}(\text{CH}_3)_3$, $\text{B}(\text{OH})_3$, AlCl_3 , GeCl_3 etc.

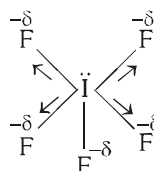


(ii) Compounds whose central atom have vacant d-orbitals and can accept one or more pair of lone electrons.

Example SF_4 , SF_6 , SnCl_2 , SnCl_4 , PX_3 , PX_5 , GeX_4 , TeX_4 , IF_5 , IF_7 , etc.



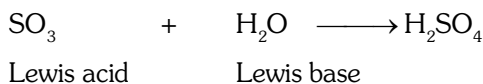
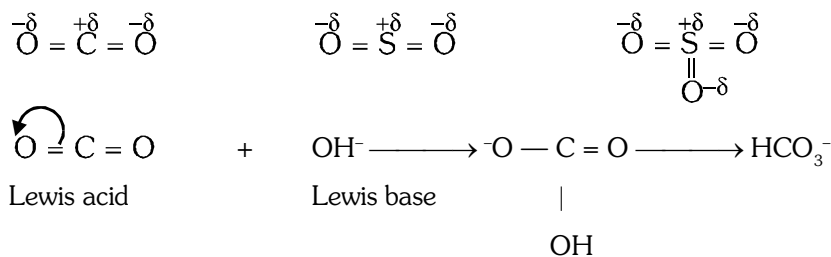
SF_6



IF_5

(iii) Molecules with a multiple bond between atoms of different electronegativities.

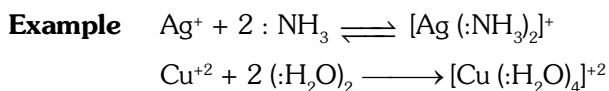
Example CO_2 , SO_2 , SO_3 etc.



(iv) **Cations :-**

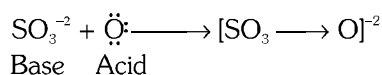
Example Ag^+ , Na^+ , Li^+ , Al^{+3} , Be^{+2} , Mg^{+2} , I^+ , Cl^+ , H^+ etc.

False cations :- Example NH_4^+ , H_3O^+ , $\text{CH}_3\text{COOH}_2^+$, PH_4^+ etc.



(v) Elements which have six electrons in their outermost shell or valence shell.

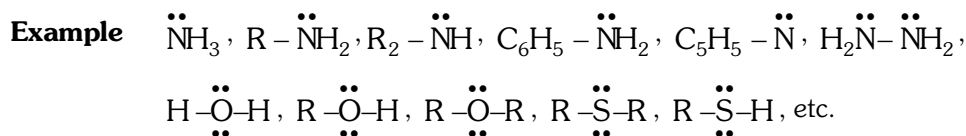
O-Family (O, S, Se, Te) Po – Radioactive element



(b) Lewis Base :- Those species which have self tendency to donate the lone pair of electrons are called bases. i.e. a base is an electron pair (lone pair) donor (nucleophile).

Classification of Lewis Bases

(i) Those species whose central atom have lone pair of electrons and have self tendency to donate them –



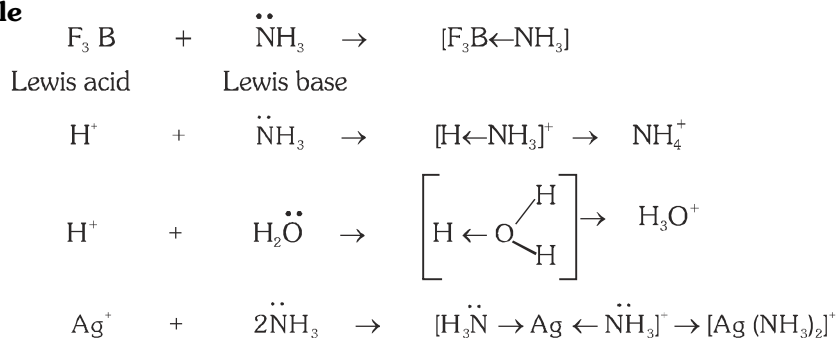
(ii) **Anions –**



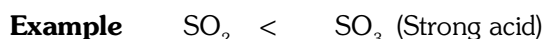
(c) Nature of water :- According to this concept nature of water is basic i.e. water is a base.

(d) Neutralisation Reaction :- According to this concept those reactions in which acid and base react together to form a co-ordinate bond between them are called neutralisation reactions.

Example



(e) Strength of acids and bases :- This concept explain the strength of acids and bases depending upon the basis of self tendency. To accept or donate the lone pair of electrons (e^-).

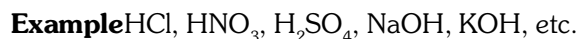


(f) Advantage :-

- This concept explains the acid and base without any solvent.
- This concept explains those acids and bases which are not explained by other concepts.

(g) Disadvantage :-

- This concept fails to explain the acid and base practically.
- According to this concept forming of co-ordinate bond in neutralisation reaction of acid and base is a slow process, whereas neutralisation reaction of acids and bases is actually fast process.
- This concept fails to explain the real acids and bases

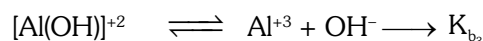
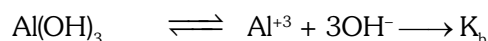


- All the lewis bases are bronsted bases but all the lewis acids are not bronsted acids.
- All Arrhenius acids are Bronsted acids but it is not so for bases.



(6) POLYACIDIC BASE AND POLYBASIC ACIDS

(a) Polyacidic Base



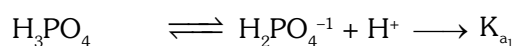
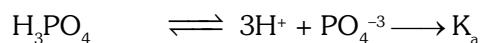
$$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$$

taking $-\log$ on both sides

$$\text{p}K_b = \text{p}K_{b_1} + \text{p}K_{b_2} + \text{p}K_{b_3}$$

$$\text{i.e. } \boxed{K_{b_1} > K_{b_2} > K_{b_3}} \Rightarrow \boxed{\text{p}K_{b_1} < \text{p}K_{b_2} < \text{p}K_{b_3}}$$

(b) Polybasic Acid



$$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$$

taking $-\log$ on both sides

$$\text{p}K_a = \text{p}K_{a_1} + \text{p}K_{a_2} + \text{p}K_{a_3}$$

$$\boxed{K_{a_1} > K_{a_2} > K_{a_3}} \Rightarrow \boxed{\text{p}K_{a_1} < \text{p}K_{a_2} < \text{p}K_{a_3}}$$

Illustrations

Illustration 33 In the dissociation, $\text{H}_2\text{A} \xrightleftharpoons{K_1} \text{H}^+ + \text{HA}^-$; $\text{HA}^- \xrightleftharpoons{K_2} \text{H}^+ + \text{A}^{2-}$

(1) K_1 is equal to K_2

(2) K_1 is smaller than K_2

(3) K_1 is greater than K_2

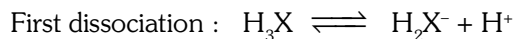
(4) K_1 is negligible

Solution.

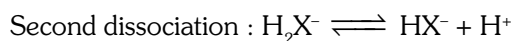
Ans. (3)

Illustration 34 Calculate the pH of 2.0×10^{-4} M H_3X Solution assuming first dissociation to be 100%, second to be 50% and third to be negligible :

Solution.



$$\therefore \text{H}^+ \text{ ion concentration} = 2 \times 10^{-4} \text{ M}$$



$$\text{H}^+ \text{ ion concentration} = C\alpha = 2 \times 10^{-4} \times 0.5$$

\therefore Third dissociation is negligible

$$\therefore [\text{H}^+] = 2 \times 10^{-4} + 10^{-4} = 3 \times 10^{-4}$$

$$\text{pH} = 4 - \log 3 = 3.52$$



BEGINNER'S BOX-5

- Which of the following is a Bronsted acid ?
 (i) HCN (ii) H_2PO_4^- (iii) NH_4^+ (iv) HCl
 (1) (i), (iii) (2) (i), (ii), (iii), (iv) (3) (ii), (iii) (4) (i), (iii), (iv)
- Which of the following is a Bronsted base ?
 (i) NH_3 (ii) CH_3NH_2 (iii) HCO_3^- (iv) SO_4^{2-}
 (1) (i), (ii), (iii), (iv) (2) (i), (ii) (3) (i), (ii), (iii) (4) (i), (iii), (iv)
- The conjugate base of hydroxide ion is—
 (1) H_2O (2) H_3O^+ (3) O^{2-} (4) O_2
- The conjugate acid of amide ion (NH_2^-) is—
 (1) N_2H_4 (2) NH_2OH (3) NH_4^+ (4) NH_3
- Which of the following can act both as a Bronsted acid as well as a Bronsted base ?
 (1) H_2SO_4 (2) HCO_3^- (3) O^{2-} (4) NH_4^+
- Which of the following acid-base reactions cannot be explained by the Bronsted theory ?
 (1) $\text{CO}_2 + \text{CaO} \longrightarrow \text{CaCO}_3$ (2) $\text{BF}_3 + \text{NH}_3 \longrightarrow \text{BF}_3^+ \text{NH}_3^-$
 (3) $\text{Ni} + 4\text{CO} \longrightarrow \text{Ni}(\text{CO})_4$ (4) All of these
- Which of the following Bronsted acid has the weakest conjugate base ?
 (1) H_2O (2) HCN (3) HCOOH (4) HF

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	1	3	4	1	1	4	4	2	1
	Que.	11									
	Ans.	2									
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7			
	Ans.	4	2	1	2	3	2	1			
	Que.	1	2	3	4	5	6				
	Ans.	2	3	2	3	1	2				
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6				
	Ans.	2	3	2	3	1	2				
	Que.	1	2	3	4	5	6				
	Ans.	3	2	3	1	4	4				
BEGINNER'S BOX-4	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			
	Que.	1	2	3	4	5	6				
	Ans.	2	1	3	4	2	4	4			



EXERCISE-I (Conceptual Questions)

INTRODUCTION

1. The formula weight of H_2SO_4 is 98. The weight of the acid in 400 mL of 0.1 M solution is:-
(1) 2.45 g (2) 3.92 g (3) 4.90 g (4) 9.8 g
2. Normality of 2M sulphuric acid is:-
(1) 2 N (2) 4N (3) N/2 (4) N/4
3. If $\text{pH} = 3.31$, then find out $[\text{H}^+]$ (Approxy)
(1) 3.39×10^{-4} (2) 5×10^{-4}
(3) 3.0×10^{-3} (4) None
4. If $[\text{OH}^-] = 5.0 \times 10^{-5} \text{ M}$ then pH will be :-
(1) $5 - \log 5$ (2) $9 + \log 5$
(3) $\log 5 - 5$ (4) $\log 5 - 9$
5. Basicity of H_3PO_3 and H_3PO_2 are respectively :-
(1) 1 and 2 (2) 2 and 3
(3) 3 and 2 (4) 2 and 1
6. Find out pH of solution having 2×10^{-3} moles of OH^- ion's in 2 litre solution :-
(1) $\text{pH} = 3$ (2) $\text{pH} = 3 + \log 2$
(3) $\text{pH} = 3 - \log 2$ (4) $\text{pH} = 11$
7. pH of tomato juice is 4.4. Then concentration of H_3O^+ will be :-
(1) 39×10^{-4} (2) 3.9×10^{-5}
(3) 3.9×10^{-4} (4) 3.9×10^5
8. 8 g NaOH is dissolved in one litre of solution, the molarity of the solution is:-
(1) 0.2 M (2) 0.4 M (3) 0.02 M (4) 0.8 M
9. The amount of acetic acid present in 100 mL of 0.1M solution is :-
(1) 0.30 g (2) 3.0 g (3) 0.60 g (4) None
10. The number of milli equivalents of acid in 100 mL of 0.5N HCl solution is:-
(1) 50 (2) 100 (3) 25 (4) 200
11. If the molar concentration of PbI_2 is $1.5 \times 10^{-3} \text{ mol L}^{-1}$, the concentration of iodide ions in g ion L^{-1} is:-
(1) 3.0×10^{-3} (2) 6.0×10^{-3}
(3) 0.3×10^{-3} (4) 0.6×10^{-6}

OSTWALD'S DILUTION LAW

12. Order of dissociation of 0.1 N CH_3COOH is :-
(Dissociation constant = 1×10^{-5})
(1) 10^{-5} (2) 10^{-4} (3) 10^{-3} (4) 10^{-2}

13. If α is the degree of dissociation of weak dibasic organic acid and y is the hydrogen ion concentration, what is the initial concentration of acid :-
(1) $\frac{\alpha(y)^{-1}}{2} \text{ M}$ (2) $y(\alpha)^{-1} \text{ M}$
(3) $\frac{y(\alpha)^{-1}}{2} \text{ M}$ (4) None of them
14. The degree of dissociation of acetic acid is given by the expression $\alpha = 0.1 \times C^{-1}$ (where C = concentration of the acid) What is the pH of the solution :-
(1) 1 (2) 2 (3) 3 (4) 4
15. Ostwald's dilution law is not applicable for strong electrolytes because:-
(1) Strong electrolytes are completely ionised
(2) Strong electrolytes are volatile
(3) Strong electrolytes are unstable
(4) Strong electrolytes often contain metal ions
16. The degree of ionisation of a compound depends upon :
(1) Size of the solute molecules
(2) Nature of the solute molecules
(3) Nature of the container taken
(4) The amount of current passed
17. Find out K_a for 10^{-2} M HCN acid, having pOH is 10 :-
(1) $K_a = 10^{-4}$ (2) $K_a = 10^{-2}$
(3) $K_a = 10^{-5}$ (4) None of them
18. Which of the following will occur if a 1.0 M solution of a weak acid is diluted to 0.01 M at constant temperature:-
(1) Percentage ionisation will increase
(2) $[\text{H}^+]$ will decrease to 0.01M
(3) K_a will increase
(4) pH will decrease by 2 units
19. The pH of 0.15 M solution of HOCl ($K_a = 9.6 \times 10^{-6}$) is:-
(1) 4.42 (2) 2.92 (3) 3.42 (4) None
20. The extent of ionisation increases (weak electrolytes)
(1) With the increase in concentration of solute
(2) On decreasing the temp. of solution
(3) On addition of excess of water to the solution
(4) On stirring the solution vigorously



21. If K_a of $\text{HCN} = 4 \times 10^{-10}$, then the pH of 2.5×10^{-1} molar HCN (aq) is:-
 (1) 4.2 (2) 4.7 (3) 0.47 (4) 5.0
22. The molarity of nitrous acid at which its pH becomes 2. ($K_a = 4.5 \times 10^{-4}$) :-
 (1) 0.3333 (2) 0.4444
 (3) 0.6666 (4) 0.2222
23. Correct statement for HCN weak acid at 25°C temperature:-
 (1) $\alpha = \frac{K_a}{[\text{H}^+]}$ (2) $\alpha = \frac{K_a \times [\text{OH}^-]}{K_w}$
 (3) (1) & (2) both (4) $K_b = C\alpha^2$

EXPLANATION OF WATER

24. Ionic product of water will increase, if :-
 (1) Dissociation the pressure
 (2) Add H^+
 (3) Add OH^-
 (4) Increase the temperature
25. For water at 25°C , 2×10^{-7} moles per litre is the correct answer for which one of the following
 (1) $[\text{H}^+] + [\text{OH}^-]$ (2) $[\text{H}^+]^2$
 (3) $[\text{OH}^-]^2$ (4) $[\text{H}^+] - [\text{OH}^-]$
26. At 25°C , the dissociation constant for pure water is given by :-
 (1) $(55.4 \times 10^{14})^{-1}$ (2) 1×10^{-14}
 (3) $\frac{1 \times 10^{-14}}{18}$ (4) None of these
27. Ionic product of water is equal to :-
 (1) Dissociation constant of water $\times [\text{H}_2\text{O}]$
 (2) Dissociation constant of water $\times [\text{H}^+]$
 (3) Product of $[\text{H}_2\text{O}]$ and $[\text{H}^+]$
 (4) Product of $[\text{OH}^-]^2$ and $[\text{H}^+]$
28. Addition of H^+ and OH^- ion's concentration at 90°C
 (1) 10^{-14} (2) 10^{-12}
 (3) 2×10^{-6} (4) 2×10^{-7}
29. At 90°C , pure water has $[\text{H}_3\text{O}^+] = 10^{-6.7} \text{ mol L}^{-1}$ what is the value of K_w at 90°C :-
 (1) 10^{-6} (2) 10^{-12}
 (3) 10^{-67} (4) $10^{-13.4}$
30. At 373 K, temp. the pH of pure H_2O can be:-
 (1) < 7 (2) > 7 (3) $= 7$ (4) $= 0$

31. The common ion effect is shown by which of the following sets of solutions :-
 (1) $\text{BaCl}_2 + \text{Ba}(\text{NO}_3)_2$ (2) $\text{NaCl} + \text{HCl}$
 (3) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ (4) None
32. Basic strength of NH_4OH in presence of NH_4Cl
 (1) Increases
 (2) Remains unchanged
 (3) Decreases
 (4) Some times increases or sometimes decreases
33. Which of the following is a true statement :
 (1) The ionisation constant and ionic product of water are same.
 (2) Water is a strong electrolyte.
 (3) The value of ionic product of water is less than that of its ionisation constant.
 (4) At 298K, the number of H^+ ions in a litre of water is 6.023×10^{16} .
34. If it is known that H_2S is a weak acid and it is ionised into 2H^+ and S^{2-} . Then in this solution HCl is added so, pH becomes less, then what will happen :-
 (1) Decrease in S^{2-} ion concentration
 (2) Concentration of S^{2-} is not affected
 (3) Increase in S^{2-} ion concentration
 (4) It is not possible, to add HCl in solution

SALTS, TYPES OF SALT & CONJUGATE THEORY

35. Which of the following is not an acidic salt :-
 (1) NaHSO_4 (2) HCOONa
 (3) NaH_2PO_3 (4) None of them
36. Which is a basic salt :-
 (1) PbS (2) PbCO_3
 (3) PbSO_4 (4) $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$
37. The process of neutralisation invariably results in the production of :-
 (1) H^+ ions
 (2) OH^- ions
 (3) Both H^+ and OH^- ions
 (4) Molecules of water
38. Which of the following is an acid salt :-
 (1) Na_2S (2) Na_2SO_3
 (3) NaHSO_3 (4) Na_2SO_4
39. The mixed salt among the following is :-
 (1) $\text{CH}(\text{OH})\text{COONa}$ (2) NaKSO_4
 (3) CaCl_2 (4) All



HYDROLYSIS OF SALTS

- 40.** At 90°C, the pH of 0.1M NaCl aqueous solution is :-
 (1) < 7 (2) > 7 (3) 7 (4) 0.1
- 41.** What will be the pH of 1.0 M ammonium formate solution, If $K_a = 1 \times 10^{-4}$ acid $K_b = 1 \times 10^{-5}$:-
 (1) 6.5 (2) 7.5 (3) 8.0 (4) 9.0
- 42.** Which salt will not undergo hydrolysis :-
 (1) KCl (2) Na_2SO_4 (3) NaCl (4) All
- 43.** Maximum efficiency of cationic hydrolysis will be shown by :-
 (1) Al^{3+} (2) Ga^{3+} (3) Tl^{+1} (4) Tl^{+3}
- 44.** $\text{HCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCOOH} + \text{OH}^-$ is related :-
 (1) $h = \sqrt{K_h}$ (2) $h = \sqrt{\frac{K_h}{C}}$
 (3) $h = \sqrt{\frac{K_h}{V}}$ (4) $K_h = \sqrt{hc}$
- 45.** The pH of aqueous solution of sodium acetate is
 (1) 7 (2) Very low
 (3) > 7 (4) < 7
- 46.** If $\text{p}K_b$ for CN^- at 25°C is 4.7. The pH of 0.5M aqueous NaCN solution is :-
 (1) 12 (2) 10 (3) 11.5 (4) 11
- 47.** The highest pH value is of :-
 (1) 0.1 M NaCl
 (2) 0.1 M NH_4Cl
 (3) 0.1 M CH_3COONa
 (4) 0.1 M $\text{CH}_3\text{COONH}_4$
- 48.** pH of K_2S solution is :-
 (1) 7 (2) Less than 7
 (3) More than 7 (4) 0
- 49.** For anionic hydrolysis, pH is given by :-
 (1) $\text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log c$
 (2) $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$
 (3) $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$
 (4) None of above
- 50.** A weak acid react with strong base, ionisation constant of weak acid is 10^{-4} . Find out equilibrium constant for this reaction :-
 (1) 10^{-10} (2) 10^{10} (3) 10^{-9} (4) 10^9
- 51.** Hydroxyl ion concentration $[\text{OH}^-]$ in the case of sodium acetate can be expressed as (where K_a is dissociation constant of CH_3COOH and C is the concentration of sodium acetate) :-
 (1) $[\text{OH}^-] = (\text{CK}_w \cdot K_a)^{1/2}$ (2) $[\text{OH}^-] = \text{C} \cdot K_w \sqrt{K_a}$
 (3) $[\text{OH}^-] = \left(\frac{\text{C} \cdot K_w}{K_a} \right)^{1/2}$ (4) $[\text{OH}^-] = \text{C} \cdot K_a \cdot K_w$
- 52.** Consider :-
 (a) FeCl_3 in water - Basic
 (b) NH_4Cl in water - Acidic
 (c) Ammonium acetate in water - Acidic
 (d) Na_2CO_3 in water - Basic
 Which is/are not correctly matched :-
 (1) b and d (2) b only
 (3) a and c (4) d only
- 53.** Which of the following salts undergoes hydrolysis in water :-
 (1) Na_3PO_4 (2) CH_3COONa
 (3) NaNO_3 (4) Both of (1) and (2)
- 54.** A salt 'X' is dissolved in water of pH = 7. The resulting solution becomes alkaline in nature. The salt is made up of :-
 (1) A strong acid and strong base
 (2) A strong acid and weak base
 (3) A weak acid and weak base
 (4) A weak acid and strong base
- 55.** K_a for cyano acetic acid is 3.5×10^{-3} . Then the degree of hydrolysis of 0.05 M. sodium cyano acetate solution will have the following value :-
 (1) 4.559×10^{-6} (2) 5.559×10^{-6}
 (3) 6.559×10^{-6} (4) 7.559×10^{-6}
- 56.** Degree of Hydrolysis of $\frac{N}{100}$ solution of KCN is
 (Given $K_a = 1.4 \times 10^{-9}$)
 (1) 2.7×10^{-3} (2) 2.7×10^{-2}
 (3) 2.7×10^{-4} (4) 2.7×10^{-5}

SOLUBILITY & SOLUBILITY PRODUCT (K_{sp})

- 57.** The solubility product of sparingly soluble univalent salt is defined as the product of ionic concentration in a :-
 (1) 1 M solution
 (2) Concentration solution
 (3) Very dilute solution
 (4) Saturated solution



58. In solubility of salts M_2X , QY_2 and PZ_2 equal, then the relation between their K_{sp} will be :-
 (1) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_2)$
 (2) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_2)$
 (3) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_2)$
 (4) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_2)$
59. The expression of solubility product of mercurous iodide is :-
 (1) $[2 \text{Hg}^{+}]^2 \times 2 [\text{I}^-]^2$ (2) $[\text{Hg}^{2+}]^2 \times [2\text{I}^-]^2$
 (3) $[\text{Hg}_2^{2+}] \times [\text{I}^-]^2$ (4) $[\text{Hg}^{2+}]^2 \times [\text{I}^-]^2$
60. At 25°C , the K_{sp} value of AgCl is 1.8×10^{-10} . If 10^{-5} moles of Ag^+ are added to solution then K_{sp} will be :-
 (1) 1.8×10^{-15} (2) 1.8×10^{-10}
 (3) 1.8×10^{-5} (4) 18×10^{-10}
61. At 25°C , required volume of water, to dissolve 1g BaSO_4 ($K_{sp} = 1.1 \times 10^{-10}$) will be (Molecular weight of $\text{BaSO}_4 = 233$) :-
 (1) 820 L. (2) 1 L.
 (3) 205 L. (4) 430 L.
62. Concentration of Ag^+ ions in saturated solution of Ag_2CrO_4 at 20°C is $1.5 \times 10^{-4} \text{ mol L}^{-1}$. At 20°C , the solubility product of Ag_2CrO_4 is :-
 (1) 3.3750×10^{-12} (2) 1.6875×10^{-10}
 (3) 1.68×10^{-12} (4) 1.6875×10^{-11}
63. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre saturated solution? solubility product of CaC_2O_4 is $2.5 \times 10^{-9} \text{ mol}^2 \text{ L}^{-2}$ and its molecular weight is 128.
 (1) 0.0064 g (2) 0.0128 g
 (3) 0.0032 g (4) 0.0640 g
64. If the concentration of CrO_4^{2-} ion in a saturated solution of silver chromate will be $2 \times 10^{-4} \text{ M}$, solubility product of silver chromate will be -
 (1) 4×10^{-8} (2) 8×10^{-12}
 (3) 32×10^{-12} (4) 6×10^{-12}
65. If the solubility of AgCl (formula mass=143) in water at 25°C is $1.43 \times 10^{-4} \text{ g/100 mL}$ of solution then the value of K_{sp} will be :-
 (1) 1×10^{-5} (2) 2×10^{-5}
 (3) 1×10^{-10} (4) 2×10^{-10}
66. If the salts M_2X , QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as - ($S < 1$)
 (1) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$
 (2) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
 (3) $K_{sp}(M_2X) = K_{sp}(QY_2) > K_{sp}(PZ_3)$
 (4) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$
67. The solubility product of As_2S_3 is given by the expression :-
 (1) $K_{sp} = [\text{As}^{3+}] \times [\text{S}^{2-}]$ (2) $K_{sp} = [\text{As}^{3+}]^1 [\text{S}^{2-}]^1$
 (3) $K_{sp} = [\text{As}^{3+}]^3 [\text{S}^{2-}]^2$ (4) $K_{sp} = [\text{As}^{3+}]^2 [\text{S}^{2-}]^3$
68. If the solubility of PbBr_2 is 'S' g molecules per litre, considering 100% ionisation its solubility product is :-
 (1) 2S^3 (2) 4S^2 (3) 4S^3 (4) 2S^4
69. If the solubility of lithium sodium hexafluoroaluminate $\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$ is 'S' mol L^{-1} . Its solubility product is equal to :-
 (1) S^8 (2) 12S^3
 (3) 18S^3 (4) 2916S^8
70. One litre of saturated solution of CaCO_3 is evaporated to dryness, when 7.0 g of residue is left. The solubility product for CaCO_3 is:-
 (1) 4.9×10^{-3} (2) 4.9×10^{-5}
 (3) 4.9×10^{-9} (4) 4.9×10^{-7}

APPLICATION OF SOLUBILITY PRODUCT(K_{sp})

71. At 30°C , In which of the one litre solution, the solubility of Ag_2CO_3 (solubility product = 8×10^{-12}) will be maximum :-
 (1) 0.05 M Na_2CO_3 (2) Pure water
 (3) 0.05 M AgNO_3 (4) 0.05 M NH_3
72. Solubility of AgBr will be minimum in :-
 (1) Pure water (2) 0.1 M CaBr_2
 (3) 0.1 M NaBr (4) 0.1 M AgNO_3
73. In which of the following, the solution of AgSCN will be unsaturated :-
 (1) $[\text{Ag}^+][\text{SCN}^-] = K_{sp}$ (2) $[\text{Ag}^+] \times [\text{SCN}^-] < K_{sp}$
 (3) $[\text{Ag}^+] \times [\text{SCN}^-] > K_{sp}$ (4) $[\text{Ag}^+][\text{SCN}^-]^2 < K_{sp}$
74. If 's' and 'S' are respectively solubility and solubility product of a sparingly soluble binary electrolyte then :-
 (1) $s = S$ (2) $s = S^2$
 (3) $s = S^{1/2}$ (4) $s = \frac{1}{2}S$
75. The solubility product of CuS , Ag_2S and HgS are 10^{-37} , 10^{-44} and 10^{-54} respectively. The solubility of these sulphides will be in the order
 (1) $\text{HgS} > \text{Ag}_2\text{S} > \text{CuS}$ (2) $\text{Ag}_2\text{S} > \text{HgS} > \text{CuS}$
 (3) $\text{CuS} > \text{Ag}_2\text{S} > \text{HgS}$ (4) $\text{Ag}_2\text{S} > \text{CuS} > \text{HgS}$
76. If the maximum concentration of PbCl_2 in water is 0.01 M at 298 K, Its maximum concentration in 0.1 M NaCl will be:-
 (1) $4 \times 10^{-3} \text{ M}$ (2) $0.4 \times 10^{-4} \text{ M}$
 (3) $4 \times 10^{-2} \text{ M}$ (4) $4 \times 10^{-4} \text{ M}$



77. M_2SO_4 (M^+ is a monovalent metal ion) has a K_{sp} of 1.2×10^{-5} at 298 K. The maximum concentration of M^+ ion that could be attained in a saturated solution of this solid at 298 K is :-
 (1) 3.46×10^{-3} M (2) 2.89×10^{-2} M
 (3) 2.8×10^{-3} M (4) 7.0×10^{-3} M
78. Which of the following has maximum solubility (K_{sp} value is given in brackets) :-
 (1) HgS (1.6×10^{-54}) (2) $PbSO_4$ (1.3×10^{-8})
 (3) ZnS (7.0×10^{-26}) (4) $AgCl$ (1.7×10^{-10})
79. Maximum soluble is :- (K_{sp} is given)
 (1) CuS (8.5×10^{-36}) (2) CdS (3.6×10^{-28})
 (3) ZnS (1.2×10^{-28}) (4) MnS (1.4×10^{-10})
80. In which of the following, the solubility of $AgCl$ will be maximum :-
 (1) 0.1 M $AgNO_3$ (2) Water
 (3) 0.1 M $NaCl$ (4) 0.1 M KCl
81. The solubility product of three sparingly soluble salts are given below :
- | No. | Formula | Solubility product |
|-----|---------|-----------------------|
| 1 | PQ | 4.0×10^{-20} |
| 2 | PQ_2 | 3.2×10^{-14} |
| 3 | PQ_3 | 2.7×10^{-35} |
- The correct order of decreasing molar solubility is:-
 (1) 1, 2, 3 (2) 2, 1, 3 (3) 3, 2, 1 (4) 2, 3, 1
82. The K_{sp} value for $Gd(OH)_3$ is 2.8×10^{-23} , the pH of $Gd(OH)_3$ in saturated solution :-
 (1) 6.08 (2) 5.08 (3) 8.47 (4) 4.08
83. If the solubility product of $AgBrO_3$ and Ag_2SO_4 are 5.5×10^{-5} and 2×10^{-5} respectively, the relationship between the solubilities of these can be correctly represented as:-
 (1) $s_{AgBrO_3} > s_{Ag_2SO_4}$
 (2) $s_{AgBrO_3} = s_{Ag_2SO_4}$
 (3) $s_{AgBrO_3} < s_{Ag_2SO_4}$
 (4) Can't predict
84. 0.5 M HCl solution has ions- Hg^{++} , Cd^{++} , Sr^{++} , Fe^{++} , Cu^{++} . To pass the H_2S gas in this solution, which are precipitated out :-
 (1) Cd^{+2} , Fe^{+2} , Sr^{+2} (2) Cd^{+2} , Hg^{+2} , Cu^{+2}
 (3) Hg^{+2} , Cu^{+2} , Fe^{+2} (4) Cu^{+2} , Sr^{+2} , Fe^{+2}
85. Solubility product of $Mg(OH)_2$ is 1×10^{-11} . At what pH, precipitation of $Mg(OH)_2$ will begin from 0.1 M Mg^{2+} solution :-
 (1) 9 (2) 5 (3) 3 (4) 7
86. A solution, containing 0.01 M Zn^{+2} and 0.01 M Cu^{2+} is saturated by passing H_2S gas. The S^{-2} concentration is 8.1×10^{-21} M, K_{sp} for ZnS and CuS are 3.0×10^{-22} and 8.0×10^{-36} respectively. Which of the following will occur in the solution:-
 (1) ZnS will precipitate
 (2) CuS will precipitate
 (3) Both ZnS and CuS will precipitate
 (4) Both Zn^{2+} and Cu^{2+} will remain in the solution
87. Consider (i) $Zn(OH)_2$ (ii) $Cr(OH)_3$ (iii) $Mg(OH)_2$ (iv) $Al(OH)_3$ which hydroxide is precipitated by NH_4OH containing NH_4Cl :-
 (1) i, ii (2) ii, iv
 (3) Only iv (4) i, ii, iii and iv
88. What will happen if the pH of the solution of 0.001 M $Mg(NO_3)_2$ solution is adjusted to pH = 9 ($K_{sp} Mg(OH)_2 = 8.9 \times 10^{-12}$)
 (1) ppt will take place
 (2) ppt will not take place
 (3) Solution will be saturated
 (4) None of these
89. The solubility product constant K_{sp} of $Mg(OH)_2$ is 9.0×10^{-12} . If a solution is 0.010 M with respect to Mg^{2+} ion, what is the maximum hydroxide ion concentration which could be present without causing the precipitation of $Mg(OH)_2$:-
 (1) 1.5×10^{-7} M (2) 3.0×10^{-7} M
 (3) 1.5×10^{-5} M (4) 3.0×10^{-5} M
90. When HCl gas is passed through a saturated solution of common salt, pure $NaCl$ is precipitated because:-
 (1) The impurities dissolve in HCl
 (2) HCl is slightly soluble in water
 (3) The ionic product $[Na^+] \times [Cl^-]$ exceeds the solubility product of $NaCl$
 (4) The solubility product of $NaCl$ is lowered by Cl^- from aq. HCl
91. A solution is a mixture of 0.06 M KCl and 0.06 M KI . $AgNO_3$ solution is being added drop by drop till $AgCl$ starts precipitating ($K_{sp} AgCl = 1 \times 10^{-10}$ and $K_{sp} AgI = 4 \times 10^{-16}$). The concentration of Iodide ion at this stage will be nearly equal to :-
 (1) 4.0×10^{-5} M (2) 2.4×10^{-7} M
 (3) 2.0×10^{-8} M (4) 4×10^{-8} M
92. Why only As^{3+} gets precipitated as As_2S_3 and not Zn^{2+} as ZnS when H_2S is passed through an acidic solution containing As^{3+} and Zn^{2+} :-
 (1) Enough As^{3+} are present in acidic medium
 (2) Zinc salt does not ionise in acidic medium
 (3) Solubility product of As_2S_3 is less than that of ZnS
 (4) Solubility product changes in presence of an acid



93. H_2S is passed through a solution of cations in HCl medium to precipitate cation of :-
 (1) II-A group of cation analysis
 (2) II - B group of cation analysis
 (3) IV group of cation analysis
 (4) Both II - A and II-B gps.
94. To have more sulphide ion concentration, H_2S should be passed through :-
 (1) 1 N HCl solution
 (2) 0.1 M HCl solution
 (3) A neutral solution such as water
 (4) An ammoniacal solution
95. The solubility product of hydroxides of Mg^{+2} , Zn^{+2} , and Fe^{+3} decreases as
 $K_{\text{sp}} \text{Mg}(\text{OH})_2 > K_{\text{sp}} \text{Zn}(\text{OH})_2 > K_{\text{sp}} \text{Fe}(\text{OH})_3$ The order of precipitation of hydroxides is:-
 (1) $\text{Fe}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$
 (2) $\text{Mg}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$
 (3) $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$
 (4) $\text{Zn}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$

FEW IMPORTANT POINTS

96. Two monobasic weak acids have the same concentration of H^+ ions. What is the relationship between dissociation constant and dilution:-
 (1) $K_{\text{a}_1} V_1 = K_{\text{a}_2} V_2$ (2) $K_{\text{a}_1} V_2 = K_{\text{a}_2} V_1$
 (3) $[K_{\text{a}_1} V_1]^{\frac{1}{2}} = K_{\text{a}_2} V_2$ (4) $K_{\text{a}_1} V_1 = [K_{\text{a}_2} V_2]^{\frac{1}{2}}$
97. What is the molar concentration of chloride ion in the solution obtained by mixing 300 mL of 3.0M NaCl and 200 mL of 4.0 M solution of BaCl_2 :-
 (1) 5.0 M (2) 1.8 M
 (3) 1.6 M (4) None of these
98. The pH of a 0.1 M formic acid 0.1% dissociated is equal to 4. What will be the pH of another weak monobasic acid (same concentration) which is 1% dissociated
 (1) 2 (2) 3 (3) 1 (4) 4

pH

99. pH of water is 7. When any substance Y is dissolved in water then pH becomes 13. Substance Y is a salt of :-
 (1) Strong acid and strong base
 (2) Weak acid and weak base
 (3) Strong acid and weak base
 (4) Weak acid and strong base

100. Minimum pH is shown by aqueous solution of :-
 (1) 0.1 M BaCl_2 (2) 0.1 M $\text{Ba}(\text{NO}_3)_2$
 (3) 0.1 M BeCl_2 (4) 0.1 M $\text{Ba}(\text{OH})_2$
101. Given :-
 (a) 0.005 M H_2SO_4 (b) 0.1 M Na_2SO_4
 (c) 10^{-2} M NaOH (d) 0.01 M HCl
 Choose the correct code having same pH :-
 (1) a, c, d (2) b, d (3) a, d (4) a, c
102. What is H^+ ion concentration of 5×10^{-3} M H_2CO_3 solution having a 10% dissociation:-
 (1) 10^{-3} (2) 10^{-2}
 (3) 10^{-1} (4) 5×10^{-2}
103. A metal hydroxide of molecular formula $\text{M}(\text{OH})_4$ is 50% ionised. Its 0.0025M solution will have the pH :-
 (1) 12 (2) 2 (3) 4 (4) 11.7
104. In the following solutions, the conc. of different acids are given, which mixture of the acid has highest pH :-
 (1) $\frac{M}{10} \text{H}_2\text{SO}_4$, $\frac{M}{20} \text{HNO}_3$, $\frac{M}{10} \text{HClO}_4$
 (2) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{10} \text{HNO}_3$, $\frac{M}{20} \text{HClO}_4$
 (3) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{10} \text{HNO}_3$, $\frac{M}{40} \text{HClO}_4$
 (4) $\frac{M}{20} \text{H}_2\text{SO}_4$, $\frac{M}{5} \text{HNO}_3$, $\frac{M}{5} \text{HClO}_4$
105. If 100 mL of pH = 3 and 400 mL of pH = 3 is mixed, what will be the pH of the mixture
 (1) 3.2 (2) 3.0 (3) 3.5 (4) 2.8
106. 10^{-6} M HCl is diluted to 100 times. Its pH is :-
 (1) 6.0 (2) 8.0 (3) 6.95 (4) 9.5
107. pH of 0.001M acetic acid would be :-
 (1) 2 (2) > 3 (3) 7 (4) 14
108. At 90°C , the pH of 0.001M KOH solution will be
 (1) 3 (2) 11 (3) 5 (4) 9
109. The pH of solution is increased from 3 to 6. Its H^+ ion concentration will be :-
 (1) Reduced to half
 (2) Doubled
 (3) Reduced by 1000 times
 (4) Increased by 1000 times
110. A solution has pOH equal to 13 at 298 K. The solution will be:-
 (1) Highly acidic (2) Highly basic
 (3) Moderately basic (4) Unpredictable



- 111.** The pH of the solution containing 10 mL of a 0.1M NaOH and 10 mL of 0.05M H_2SO_4 would be
 (1) Zero (2) 1 (3) >7 (4) 7
- 112.** Which of the following statements are (is) correct
 (a) The pH of 1.0×10^{-8} M solution of HCl is 8.
 (b) The conjugate base of H_2PO_4^- is HPO_4^{2-} .
 (c) Autoprotolysis constant of water increases with temperature.
 (d) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point $\text{pH} = 1/2 \text{ pK}_a$
 (1) a (2) a, b (3) a, b, d (4) b, c
- 113.** In a solution of $\text{pH} = 5$, more acid is added in order to reduce the $\text{pH} = 2$. The increase in hydrogen ion concentration is:-
 (1) 100 times (2) 1000 times
 (3) 3 times (4) 5 times
- 114.** The hydrogen ion concentration in a given solution is 6×10^{-4} M. Its pH will be :-
 (1) 6 (2) 3.22 (3) 4 (4) 2.
- 115.** The pOH of beer is 10.0. The hydrogen ion concentration will be :-
 (a) 10^{-10} (b) $\frac{K_w}{10^{-10}}$ (c) $\frac{K_w}{10^{-8}}$ (d) 10^{-4}
 (1) a, d (2) b, c (3) a, b, c (4) None
- 116.** An aqueous solution whose $\text{pH} = 0$ is :-
 (1) Basic (2) Acidic
 (3) Neutral (4) Amphoteric
- 117.** The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-
 (1) 3.3 (2) 3.5 (3) 4.5 (4) 4.0
- 118.** Following five solution of KOH were prepared as-
 First \rightarrow 0.1 moles in 1 L
 Second \rightarrow 0.2 moles in 2 L
 Third \rightarrow 0.3 moles in 3 L
 Fourth \rightarrow 0.4 moles in 4 L
 Fifth \rightarrow 0.5 moles in 5 L
 The pH of resultant solution is :-
 (1) 2 (2) 1 (3) 13 (4) 7
- 119.** The pH of a 0.02 M ammonia solution which is 5% ionised will be :-
 (1) 2 (2) 11 (3) 5 (4) 7
- 120.** For $\frac{N}{10}$ H_2SO_4 , pH value is :-
 (1) 1 (2) 0.586 (3) 0.856 (4) None
- 121.** An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be:-
 (1) 9 (2) Between 6 and 7
 (3) 7 (4) Unpredictable
- 122.** H_2X is a dibasic acid which dissociates completely in water. Which one of the following is the molarity of an aqueous solution of this acid which has a pH of 1 :-
 (1) 0.1 (2) 0.05 (3) 0.2 (4) 0.5
- 123.** How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-
 (1) 1 (2) 0.02 (3) 0.009 (4) 0.01
- 124.** 8 g NaOH and 4.9 g H_2SO_4 are present in one litre of the solution. What is its pH
 (1) 1 (2) 13 (3) 12 (4) 2
- 125.** Calculate pH of a solution whose 100 mL contains 0.2 g NaOH dissolved in it :-
 (1) 10.699 (2) 11.699
 (3) 12.699 (4) 13.699
- 126.** One litre solution contains 1M HOCl [$K_a = 10^{-8}$] and 1 M NaOH. What is the pH of the solution :-
 (1) 8 (2) 11 (3) 5 (4) 2
- 127.** What is the quantity of NaOH present in 250 cc of the solution, so that it gives a $\text{pH} = 13$:-
 (1) 10^{-13} g (2) 10^{-1} g (3) 1.0 g (4) 4.0 g
- 128.** 0.001 mol of the strong electrolyte $\text{M}(\text{OH})_2$ has been dissolved to make a 20 mL of its saturated solution. Its pH will be :- [$K_w = 1 \times 10^{-14}$]
 (1) 13 (2) 3.3 (3) 11 (4) 9.8
- 129.** Choose the wrong statement :-
 (1) For a neutral solution : $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$
 (2) For an acidic solution : $[\text{H}^+] > \sqrt{K_w}$ and $[\text{OH}^-] < \sqrt{K_w}$
 (3) For a basic solution : $[\text{H}^+] < \sqrt{K_w}$ and $[\text{OH}^-] > \sqrt{K_w}$
 (4) For a neutral solution at all temperatures : $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ M
- 130.** The pH of 0.1 M solution of the following salts increases in order :-
 (1) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$
 (2) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$
 (3) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
 (4) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$



BUFFER SOLUTIONS and INDICATOR

- 131.** In a buffer solution the ratio of concentration of NH_4Cl and NH_4OH is 1 : 1 when it changes in 2 : 1 what will be the value of pH of buffer :-
(1) Increase (2) Decrease
(3) No effect (4) N.O.T.
- 132.** To a 50 mL of 0.05M formic acid how much volume of 0.10M sodium formate must be added to get a buffer solution of pH = 4.0 ? (pK_a of the acid is 3.8)
(1) 50 mL (2) 4 mL (3) 39.6 mL (4) 100 mL
- 133.** In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-
(1) NaOH (2) RbOH
(3) KOH (4) NH_4OH
- 134.** In a mixture of weak acid and its salt, the ratio of concentration of acid to salt is increased ten-fold. The pH of the solution :-
(1) Decreases by one (2) Increases by one-tenth
(3) Increases by one (4) Increases ten-fold
- 135.** pK_b for NH_4OH at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of NH_4OH and NH_4Cl will be:-
(1) 7.74 (2) 4.74 (3) 2.37 (4) 9.26
- 136.** What is the suitable indicator for titration of NaOH and oxalic acid:-
(1) Methyl orange (2) Methyl red
(3) Phenolphthalein (4) Starch solution
- 137.** Phenolphthalein does not act as an indicator for the titration between :-
(1) KOH and H_2SO_4
(2) NaOH and CH_3COOH
(3) Oxalic acid and KMnO_4
(4) $\text{Ba}(\text{OH})_2$ and HCl
- 138.** Which can act as buffer :-
(1) $\text{NH}_4\text{OH} + \text{NaOH}$
(2) $\text{HCOOH} + \text{CH}_3\text{COONa}$
(3) 40 mL 0.1 M NaCN + 20 mL of 0.1 M HCl
(4) None of them
- 139.** The buffer solution play an important role in :-
(1) Increasing the pH value
(2) Decreasing the pH value
(3) Keeping the pH constant
(4) Solution will be neutral
- 140.** K_a for HCN is 5×10^{-10} at 25°C . For maintaining a constant pH of 9, the volume of 5M KCN solution required to be added to 10mL of 2M HCN solution is-
(1) 4 mL (2) 7.95 mL
(3) 2 mL (4) 9.3 mL
- 141.** Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to -
(1) 1.0 (2) 100.0 (3) 10.0 (4) 0.1
- 142.** The pink colour of phenolphthalein in alkaline medium is due to -
(1) Negative ion (2) Positive ion
(3) OH^- ions (4) Neutral form
- 143.** Which indicator works in the pH range 8 – 9.8
(1) Phenolphthalein (2) Methyl orange
(3) Methyl red (4) Litmus
- 144.** A basic - buffer will obey the equation $\text{pOH} - \text{pK}_b = 1$ only under condition:-
(1) [Conjugate acid] : [base] = 1 : 10
(2) [Conjugate acid] = [base]
(3) [Conjugate acid] : [base] = 10 : 1
(4) N.O.T
- 145.** For weak acid strong base titration, the indicator used is :-
(1) Potassium di-chromate
(2) Methyl orange
(3) Litmus
(4) Phenolphthalein
- 146.** From the following in which titration methyl orange is a best indicator :-
(1) $\text{CH}_3\text{COOH} + \text{NaOH}$ (2) $\text{H}_2\text{C}_2\text{O}_4 + \text{NaOH}$
(3) $\text{HCl} + \text{NaOH}$ (4) $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$
- 147.** The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are :-
(1) 3 (2) 1 (3) 2 (4) 0
- 148.** The H^+ ion concentration in 0.001 M acetic acid is $1.34 \times 10^{-4} \text{ g ion L}^{-1}$. The H^+ ion concentration of 0.164 g of CH_3COONa is added to a litre of 0.001 M CH_3COOH will be :-
(1) 9×10^{-6} (2) 18×10^{-6}
(3) 4.5×10^{-6} (4) 5×10^{-6}
- 149.** A certain acidic buffer solution contains equal concentration of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is :-
(1) 4 (2) 7 (3) 10 (4) 14
- 150.** When 1.0 mL of dil. HCl acid is added to 100 mL of a buffer solution of pH 4.0. The pH of the solution
(1) Becomes 7 (2) Does not change
(3) Becomes 2 (4) Becomes 10
- 151.** The pH of blood is maintained by CO_2 and H_2CO_3 in the body and chemical constituents of blood. This phenomenon is called :-
(1) Colloidal (2) Buffer action
(3) Acidity (4) Salt balance



- 152.** Phenolphthalein is not a good indicator for titrating
 (1) NaOH against oxalic acid
 (2) NaOH against HCl
 (3) NaOH against H_2SO_4
 (4) Ferrous sulphate against KMnO_4
- 153.** Which of the following solutions does not act as buffer :-
 (1) $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$
 (2) $\text{NaHCO}_3 + \text{H}_2\text{CO}_3$
 (3) $\text{NH}_4\text{Cl} + \text{HCl}$
 (4) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- 154.** 50 mL of 2N acetic acid mixed with 10 mL of 1N sodium acetate solution will have an approximate pH of ($K_a = 10^{-5}$) :-
 (1) 4 (2) 5 (3) 6 (4) 7
- 155.** On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralised. If $\text{p}K_a$ of CH_3COOH is 4.7 then the pH of the resulting solution is :-
 (1) More than 4.7 but less than 5.0
 (2) Less than 4.7 but more than 4.0
 (3) More than 5.0
 (4) Remains unchanged
- 156.** 500 mL of 0.2 M acetic acid are added to 500 mL of 0.30 M sodium acetate solution. If the dissociation constant of acetic acid is 1.5×10^{-5} then pH of the resulting solution is:-
 (1) 5.0 (2) 9.0 (3) 3.0 (4) 4.0
- 157.** Half of the formic acid solution is neutralised on addition of a KOH solution to it. If $K_a(\text{HCOOH}) = 2 \times 10^{-4}$ then pH of the solution is : ($\log 2 = 0.3010$)
 (1) 3.6990 (2) 10.3010 (3) 3.85 (4) 4.3010
- 158.** A solution contains 0.2M NH_4OH and 0.2M NH_4Cl . If 1.0 mL of 0.001 M HCl is added to it. What will be the $[\text{OH}^-]$ of the resulting solution [$K_b = 2 \times 10^{-5}$] :-
 (1) 2×10^{-5} (2) 5×10^{-10}
 (3) 2×10^{-3} (4) None of these
- 159.** Henderson equation $\text{pH} - \text{p}K_a = 1$ will be applicable to an acidic buffer when :-
 (1) $[\text{Acid}] = [\text{Conjugate base}]$
 (2) $[\text{Acid}] \times 10 = [\text{Conjugate base}]$
 (3) $[\text{Acid}] = [\text{Conjugate base}] \times 10$
 (4) None of these
- 160.** 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the OH^- ion concentration of this solution: $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$
 (1) 3.0×10^{-3} (2) 9.0×10^{-4}
 (3) 9.0×10^{-3} (4) 3.0×10^{-4}
- 161.** When 0.02 moles of NaOH are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-
 (1) 0.4 (2) 0.05 (3) - 0.05 (4) 2.5
- 162.** Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl . K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$:-
 (1) 8.1187 (2) 9.8117
 (3) 8.8117 (4) None of these
- 163.** What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 1.34 \times 10^{-5}$ at 25°C) to obtain a buffer solution of pH 4.75 :-
 (1) 4.52×10^{-2} M (2) 3.52×10^{-2} M
 (3) 2.52×10^{-2} M (4) 1.52×10^{-2} M
- 164.** What will be the pH of the solution, if 0.01 moles of HCl is dissolved in a buffer solution containing 0.02 moles of propanoic acid ($K_a = 1.34 \times 10^{-5}$) and 0.0152 moles of salt, at 25°C : $[\log(0.173) = -0.76]$
 (1) 3.11 (2) 4.11 (3) 5.11 (4) 6.11
- 165.** Calculate the pH of a buffer solution prepared by dissolving 30g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1M HCl. K_a for $\text{HCO}_3^- = 5.63 \times 10^{-11}$ $\left[\log\left(\frac{133}{150}\right) = -0.05 \right]$
 (1) 8.197 (2) 9.197
 (3) 10.197 (4) 11.197
- 166.** Calculate the ratio of pH of a solution containing 1 mole of $\text{CH}_3\text{COONa} + 1$ mole of HCl per litre and of other solution containing 1 mole $\text{CH}_3\text{COONa} + 1$ mole of acetic acid per litre :-
 (1) 1 : 1 (2) 2 : 1 (3) 1 : 2 (4) 2 : 3
- 167.** When 20 mL of $\frac{M}{20}$ NaOH are added to 10 mL of $\frac{M}{10}$ HCl, the resulting solution will:-
 (1) Turn blue litmus red
 (2) Turn phenolphthalein solution
 (3) Turn methyl orange red
 (4) Will have no effect on either red or blue litmus
- 168.** 10 mL of a solution contains 0.1 M $\text{NH}_4\text{Cl} + 0.01$ M NH_4OH . Which addition would not change the pH of solution :-
 (1) Adding 1 mL water
 (2) Adding 5 mL of 0.1 M NH_4Cl
 (3) Adding 5 mL of 0.1 M NH_4OH
 (4) Adding 10 mL of 0.1 M NH_4Cl



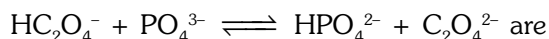
169. $\frac{N}{10}$ acetic acid was titrated with $\frac{N}{10}$ NaOH. When 25%, 50% and 75% of titration is over then the pH of the solution will be :- [$K_a = 10^{-5}$]
 (1) $5 + \log 1/3$, 5, $5 + \log 3$
 (2) $5 + \log 3$, 4, $5 + \log 1/3$
 (3) $5 - \log 1/3$, 5, $5 - \log 3$
 (4) $5 - \log 1/3$, 4, $5 + \log 1/3$

ACID AND BASE

170. The conjugated acid of O^{2-} ion's is :-
 (1) O_2^+ (2) H^+ (3) H_3O^+ (4) OH^-
171. Ionization constant of AOH and BOH base are K_{b1} and K_{b2} . Their relation is $pK_{b1} < pK_{b2}$. Conjugate of following base, does not show maximum pH :
 (1) AOH (2) BOH
 (3) Both of them (4) NOT
172. Select the species which can function as - Lewis base, bronsted acid and bronsted base:-
 (a) H_2O (b) NH_4^+ (c) N^{3-}
 Correct code is :-
 (1) Only a (2) a, b (3) a, c (4) b, c
173. Which ion does not show acid behaviour :-
 (1) $[Al(H_2O)_6]^{+3}$ (2) $[Fe(H_2O)_6]^{+3}$
 (3) HPO_4^{2-} (4) ClO_3^-
174. An example of Lewis acid is:-
 (1) CaO (2) CH_3NH_2
 (3) SO_3 (4) None of these
175. In the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ water behaves as :-
 (1) Acid (2) Base
 (3) Neutral (4) Both acid & Base
176. Which acts as Lewis base in the reaction $BCl_3 + :PH_3 \rightarrow Cl_3B \leftarrow PH_3$
 (1) PH_3 (2) BCl_3
 (3) Both 1 & 2 (4) None
177. Which acts as Lewis acid in the reaction $SnCl_2 + 2Cl^- \longrightarrow [SnCl_4]^{2-}$
 (1) Cl^- (2) $SnCl_2$ (3) $SnCl_4$ (4) None
178. The conjugated base of $(CH_3)_2NH_2^+$ is :-
 (1) CH_3NH_2 (2) $(CH_3)_2N^+$
 (3) $(CH_3)_2N$ (4) $(CH_3)_2NH$
179. Which equilibrium can be described as Lewis acid base reaction but not Bronsted acid base reaction:-
 (1) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
 (2) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
 (3) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
 (4) $Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$
180. Conjugate base of hydrazoic acid is :-
 (1) HN_3^- (2) N_3^- (3) N^{3-} (4) N_2^-
181. NH_3 gas dissolves in water to give NH_4OH , in this reaction, water acts as :-
 (1) An acid (2) A base
 (3) A salt (4) A conjugate base
182. Conjugate acid of $Zn(OH)_2$ is :-
 (1) $Zn(OH)^+$ (2) $Zn(OH_3)^+$ (3) Zn^{2+} (4) None
183. When ammonia is added to water it decreases the concentration of which of the following ion
 (1) OH^- (2) H_3O^+ (3) NH_4^+ (4) None
184. The strongest acid among the following is -
 (1) $ClO_3(OH)$ (2) $ClO_2(OH)$
 (3) $SO(OH)_2$ (4) $SO_2(OH)_2$
185. Which of the following is not a Bronsted acid :-
 (1) $CH_3NH_4^+$ (2) CH_3COO^-
 (3) H_2O (4) HSO_4^-
186. Which of the following example behave as a Lewis acid BF_3 , $SnCl_2$, $SnCl_4$:-
 (1) Stanus chloride, stanic chloride
 (2) BF_3 , Stanus chloride
 (3) Only BF_3
 (4) BF_3 , stanus chloride, stanic chloride
187. In the reaction $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$, the conjugate base of HNO_3 is :-
 (1) H_2O (2) H_3O^+
 (3) NO_3^- (4) H_3O^+ and NO_3^-
188. The conjugate base of the weak acid in the reaction $HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$ is
 (1) HBr (2) H_2O (3) Br^- (4) H_3O^+
189. In the reaction, $AlCl_3 + Cl^- \rightarrow [AlCl_4]^-$, $AlCl_3$ acts as :-
 (1) Salt (2) Lewis base
 (3) Bronsted acid (4) Lewis acid
190. Mg^{2+} is ----- than Al^{3+} :-
 (1) Strong Lewis acid (2) Strong Lewis base
 (3) Weak Lewis acid (4) Weak Lewis base

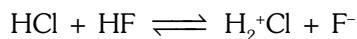


191. The two Bronsted bases in the reaction



- (1) HC_2O_4^- and PO_4^{2-}
- (2) HPO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$
- (3) PO_4^{3-} and $\text{C}_2\text{O}_4^{2-}$
- (4) HC_2O_4^- and HPO_4^{2-}

192. The compound HCl behaves as ---- in the reaction,



- (1) Strong acid
- (2) Strong base
- (3) Weak acid
- (4) Weak base

193. Which of the following is not a lewis base:-

- (1) NH_3
- (2) O^{2-}
- (3) H_2O
- (4) I^+

194. Which of the following is bronsted Lowry acid:-

- (1) SO_4^{2-}
- (2) H_3O^+
- (3) OH^-
- (4) Cl^-

195. The conjugated base for bicarbonate ion is:-

- (1) CO_3^{2-}
- (2) HCO_3^-
- (3) CO_2
- (4) H_2CO_3

196. Conjugated base of OH^- is :-

- (1) H_2O
- (2) H_3O^+
- (3) H^+
- (4) O^{2-}

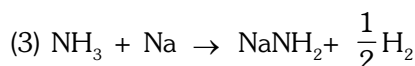
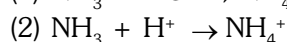
197. HCl does not behave as acid in :-

- (1) NH_3
- (2) $\text{C}_2\text{H}_5\text{OH}$
- (3) H_2O
- (4) C_6H_6

198. Which of the following is a base according to Lowry-Bronsted concept :-

- (1) I^-
- (2) H_3O^+
- (3) HCl
- (4) NH_4^+

199. In which of the following reactions NH_3 acts as acid



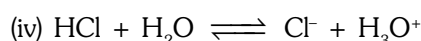
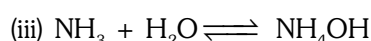
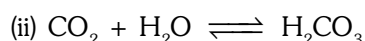
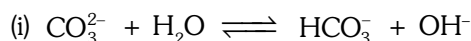
(4) NH_3 cannot act as acid

200. According to Bronsted concept, the acids in the

following reaction $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ are :-

- (1) NH_3 and NH_4^+
- (2) H_2O and OH^-
- (3) H_2O and NH_4^+
- (4) NH_3 and OH^-

201. Consider the following reactions :-



Which of the pairs of reactions proves that water is amphoteric in character :-

- (1) (i) and (ii)
- (2) (ii) and (iii)
- (3) (iii) and (iv)
- (4) (i) and (iii)

202. CH_3COO^- ion is a :-

- (1) Weak conjugate base
- (2) Strong conjugate base
- (3) Weak conjugate acid
- (4) Strong conjugate acid

203. Which of the following is strongest conjugate base

- (1) ClO_4^-
- (2) HCO_3^-
- (3) F^-
- (4) HSO_4^-

204. Which of the following species can act as Lewis base :-

- (1) Cu^{2+}
- (2) AlCl_3
- (3) NH_3
- (4) BF_3

205. A compound having the formula $\text{NH}_2\text{CH}_2\text{COOH}$ may behave :-

- (1) Only as an acid
- (2) Only as a base
- (3) Both as an acid and base
- (4) Neither acid nor base

206. BF_3 is acid according to :-

- (1) Lewis
- (2) Arrhenius
- (3) Bronsted and Lowery
- (4) Madam Curie

207. Which of the following can act both as Bronsted acid and Bronsted base :-

- (1) Na_2CO_3
- (2) O^{2-}
- (3) CO_3^{2-}
- (4) NH_3

208. The strongest conjugate base is :-

- (1) NO_3^-
- (2) Cl^-
- (3) SO_4^{2-}
- (4) CH_3COO^-

209. Aluminium chloride is :-

- (1) Bronsted Lowry acid
- (2) Arrhenius acid
- (3) Lewis acid
- (4) Lewis base

210. Water is a :-

- (1) Protogenic solvent
- (2) Protophilic solvent
- (3) Amphotropic solvent
- (4) Aprotic solvent

211. Ammonium ion is :-

- (1) A conjugate acid
- (2) A conjugate base
- (3) Neither an acid nor a basic
- (4) Both an acid and a base

212. Species which do not act both as Bronsted acid and base is :-

- (1) $(\text{HSO}_4^-)^{-1}$
- (2) Na_2CO_3
- (3) NH_3
- (4) OH^{-1}

213. Which one of the following is strong Lewis base & Bronsted acid & bronsted base:-

- (1) NH_3
- (2) PH_3
- (3) CH_4
- (4) BH_3



214. Which of the following pair is Lewis acid & Lewis base & product of these is also Lewis base

- (1) BF_3 , NH_3 (2) SiCl_4 , 2Cl^-
 (3) CH_3^\oplus , $^\ominus\text{OC}_2\text{H}_5$ (4) None of these

215. Which of the following is not a correct statement

- (1) Arrhenius theory of acids-bases is capable of explaining the acidic or basic nature of the substances in the solvents other than water
 (2) Arrhenius theory does not explain acidic nature of AlCl_3
 (3) The aqueous solution of Na_2CO_3 is alkaline although it does not contain OH^- ions
 (4) Aqueous solution of CO_2 is acidic although it does not contain H^+ ions

216. For the reaction $\text{NH}_4^+ + \text{S}^{2-} \rightleftharpoons \text{NH}_3 + \text{HS}^-$, NH_3 and S^{2-} are a group of :-

- (1) Acids (2) Bases
 (3) Acid-base pair (4) None of these

217. According to Lewis concept acid & base pair is-

- (1) HO^- , H^+ (2) Ag^+ , Cl^-
 (3) BF_3 , NH_3 (4) None of these

EXERCISE-I (Conceptual Questions)														ANSWER KEY	
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	2	2	2	4	4	2	1	3	1	1	4	3	1	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	1	2	3	4	4	3	4	1	1	1	3	4	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	4	1	2	4	4	3	2	1	1	4	1	2	3
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	3	3	3	2	3	3	4	4	4	2	4	4	3	2
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	3	1	3	3	3	4	3	4	1	4	2	2	3	4
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	4	2	2	4	2	4	3	3	2	1	2	2	2	4	3
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	2	3	4	4	1	2	1	2	4	3	3	1	4	3	2
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	3	2	4	3	1	4	4	2	2	4	2	1	3	2	1
Que.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
Ans.	2	2	3	2	3	2	3	1	4	4	2	3	4	1	4
Que.	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
Ans.	3	3	3	3	3	1	1	1	3	4	3	1	1	1	2
Que.	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165
Ans.	2	4	3	1	1	1	1	1	2	2	1	3	4	2	3
Que.	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180
Ans.	3	4	1	1	4	2	1	4	3	1	1	2	4	4	2
Que.	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195
Ans.	1	1	2	1	2	4	3	2	4	3	3	4	4	2	1
Que.	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210
Ans.	4	4	1	3	3	3	2	2	3	3	1	4	4	3	3
Que.	211	212	213	214	215	216	217								
Ans.	1	2	1	3	1	2	3								



Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** When small amount of acid or base is added to pure water, its pH undergoes a change.
Reason :- Addition of an acid or base increases the degree of ionisation of water.
 (1) A (2) B (3) C (4) D
- Assertion :-** Solubility of AgBr decreases in the presence of sodium bromide.
Reason :- Sodium bromide undergoes hydrolysis in water.
 (1) A (2) B (3) C (4) D
- Assertion :-** The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
Reason :- The ionisation of acetic acid is suppressed by the addition of sodium acetate.
 (1) A (2) B (3) C (4) D
- Assertion :-** If HCl gas is passed through saturated NaCl solution, solid NaCl starts to precipitate.
Reason :- HCl decreases the solubility product of NaCl.
 (1) A (2) B (3) C (4) D
- Assertion :-** The aqueous solution of Na_3PO_4 is alkaline in nature.
Reason :- Na_3PO_4 in its aqueous solution undergoes anionic hydrolysis.
 (1) A (2) B (3) C (4) D
- Assertion :-** If $K_{sp} < \text{ionic product}$, precipitate is formed.
Reason :- Solubility product (K_{sp}) is the highest limit of ionic product of the electrolyte in saturated solutions.
 (1) A (2) B (3) C (4) D
- Assertion :-** To precipitate the cations of fourth group in qualitative analysis, medium is made alkaline before passing H_2S gas.
Reason :- This is done to suppress the ionisation of H_2S .
 (1) A (2) B (3) C (4) D
- Assertion :-** When an acid or a base is added to water at constant temperature the pH changes.
Reason :- This is due to change in ionic product of water.
 (1) A (2) B (3) C (4) D
- Assertion :** Addition of NH_4OH to an aqueous solution of BaCl_2 in the presence of NH_4Cl (excess) precipitates $\text{Ba}(\text{OH})_2$.
Reason : $\text{Ba}(\text{OH})_2$ is insoluble in water.
 (1) A (2) B (3) C (4) D
- Assertion :-** Sb(III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
Reason :- The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation.
 (1) A (2) B (3) C (4) D
- Assertion :-** For H_2SO_4 , K_{a1} value is much greater than K_{a2} .
Reason :- H_2SO_4 is a strong acid.
 (1) A (2) B (3) C (4) D
- Assertion :-** Solubility of salt of SB and WA changes when pH of the solution is changed.
Reason :- Solubility product (K_{sp}) depends on pH.
 (1) A (2) B (3) C (4) D
- Assertion :-** A mixture of a weak acid CH_3COOH and sodium acetate forms a buffer solution.
Reason :- A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.
 (1) A (2) B (3) C (4) D
- Assertion :-** At 25°C the pH of 10^{-8} M HCl is 8.
Reason :- pH of acidic solution is always below 7 at 25°C .
 (1) A (2) B (3) C (4) D



15. **Assertion :-** In the acid base titration involving a strong base and a weak acid methyl orange can be used as an indicator.
Reason :- Methyl orange changes its colour in pH range 3 to 5.
 (1) A (2) B (3) C (4) D
16. **Assertion :-** pH of a buffer changes with temperature.
Reason :- Ionic product of water (K_w) changes with temperature.
 (1) A (2) B (3) C (4) D
17. **Assertion :-** H_3PO_3 is a dibasic compound.
Reason :- The two H-atom are directly attached to P.
 (1) A (2) B (3) C (4) D
18. **Assertion :** Boric acid behaves as a weak monobasic acid.
Reason : Boric acid contains hydrogen bonds in its structure.
 (1) A (2) B (3) C (4) D
19. **Assertion :** H_2O is amphoteric in nature.
Reason : H_2O can accept a proton to form H_3O^+ ion and can donate a proton to form OH^- ion.
 (1) A (2) B (3) C (4) D
20. **Assertion :** All Arrhenius acids are also Bronsted acids.
Reason : All Bronsted bases are also Lewis bases.
 (1) A (2) B (3) C (4) D
21. **Assertion :-** The buffer solution has a capacity to resist the change in pH value on addition of small amount of acid or base to it.
Reason :- pH value of buffer solution does not change on dilution or on keeping for long.
 (1) A (2) B (3) C (4) D
22. **Assertion :-** The species in the buffer must not react with each other.
Reason :- The pH of a buffer depends on the value of K_a of the weak acid and the relative concentration of that acid and its conjugate base.
 (1) A (2) B (3) C (4) D

23. **Assertion :-** Only a very small amount of indicator should be used.

Reason :- So that addition of the indicator does not effect the pH of the solution.

- (1) A (2) B (3) C (4) D

24. **Assertion :-** Solubility of sparingly soluble salt increases with increase in temperature.

Reason :- Enthalpy of solution is negative for all salts.

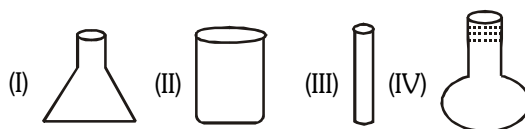
- (1) A (2) B (3) C (4) D

25. **Assertion :-** HCl is titrated with NaOH using phenolphthalein as indicator, pink colour appears in solution when OH^- ion is present in excess in solution.

Reason :- At end point, both reacting species, neutralises each other.

- (1) A (2) B (3) C (4) D

26. **Assertion :-**



II is more suitable for titration.

Reason :- It is difficult to add titrant in first.

- (1) A (2) B (3) C (4) D

27. **Assertion :** In $NaHCO_3$ solution phenolphthalein is colorless.

Reason : Phenolphthalein is colorless in basic medium and pH of $NaHCO_3$ is less than 10.

- (1) A (2) B (3) C (4) D

28. **Assertion :-** Na_2SO_3 is alkaline towards litmus.

Reason :- H_2SO_3 is formed due to hydrolysis.

- (1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	3	4	3	1	1	3	3	4	4	2	3	1	4	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	2	3	2	1	3	2	2	1	3	2	4	4	2		

